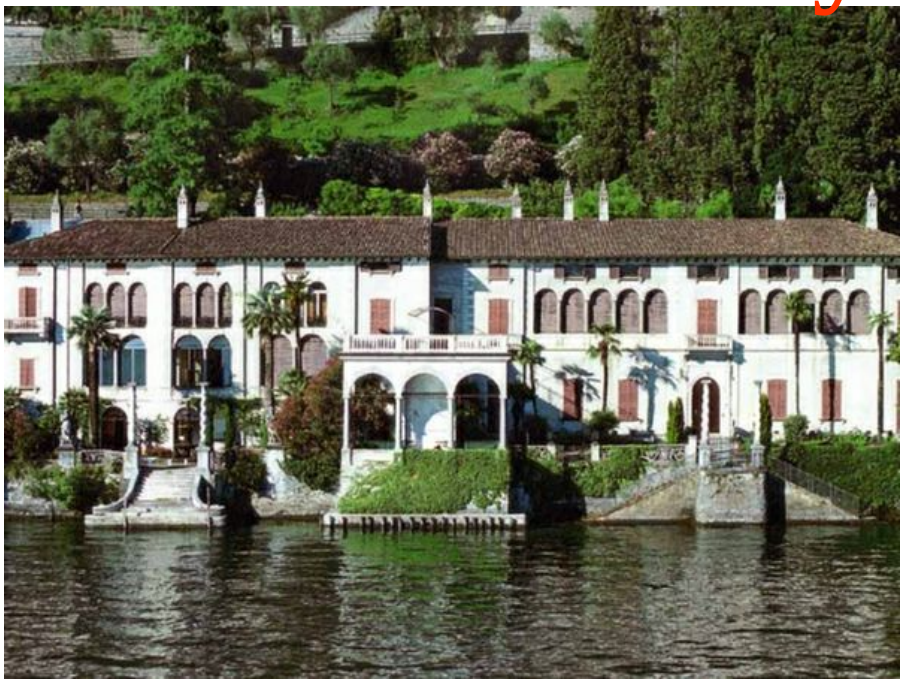
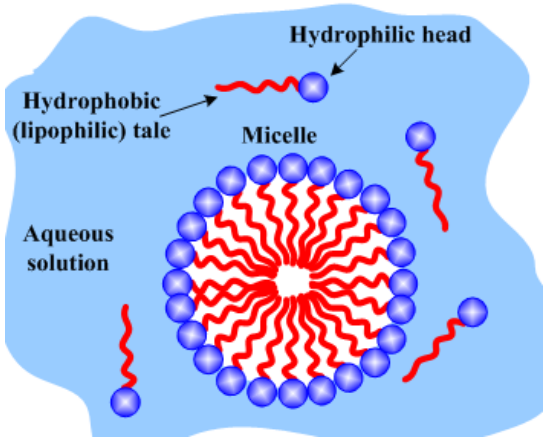
Short Course on Polymer Physics of Self-Assembly

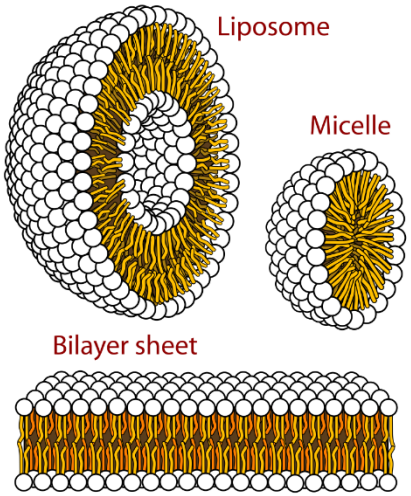


Audience Participation is Required

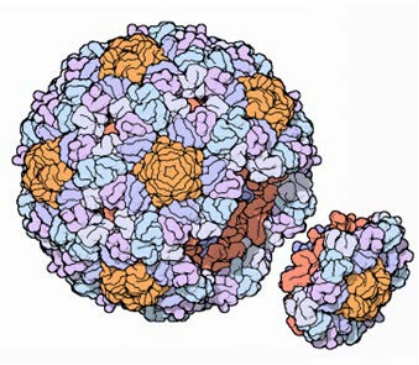
Examples of Self-Assembly



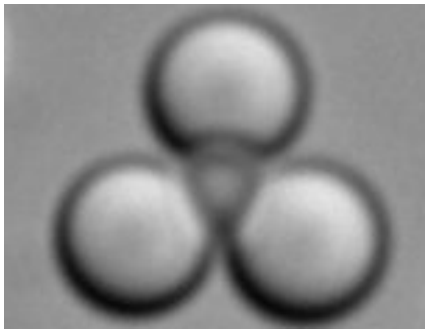
surfactants



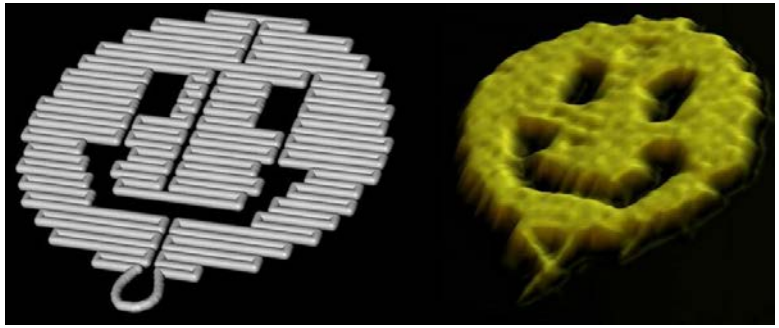
lipids



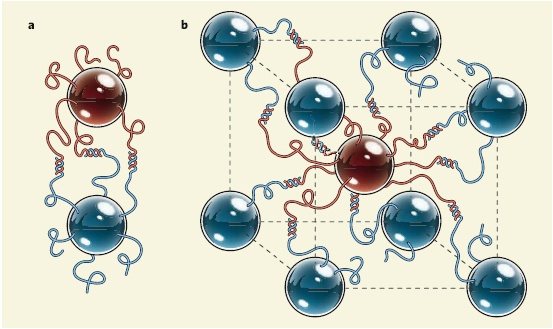
proteins



colloids

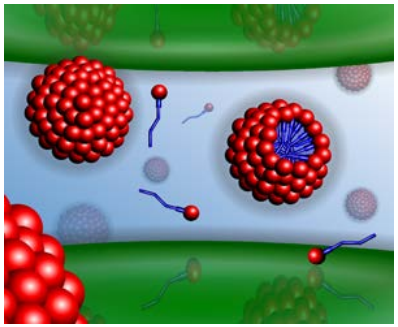


DNA origami



DNA-colloidal assembly

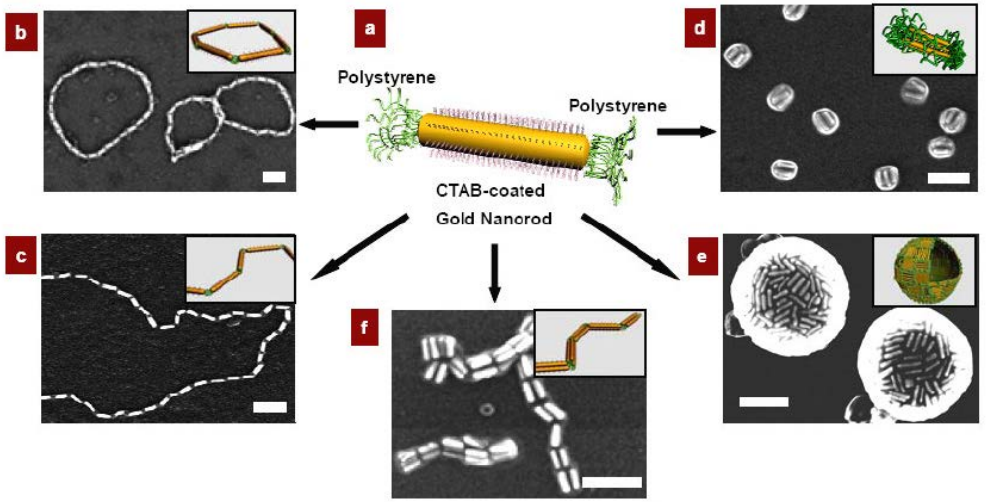
Self-Assembly of Polymers



surfactants

Need to understand repulsion of **lyophilic block**, attraction of **lyophobic block** and **interfacial energy** to design and control self-assembly of polymeric micelles.

Polymer-driven colloidal assembly

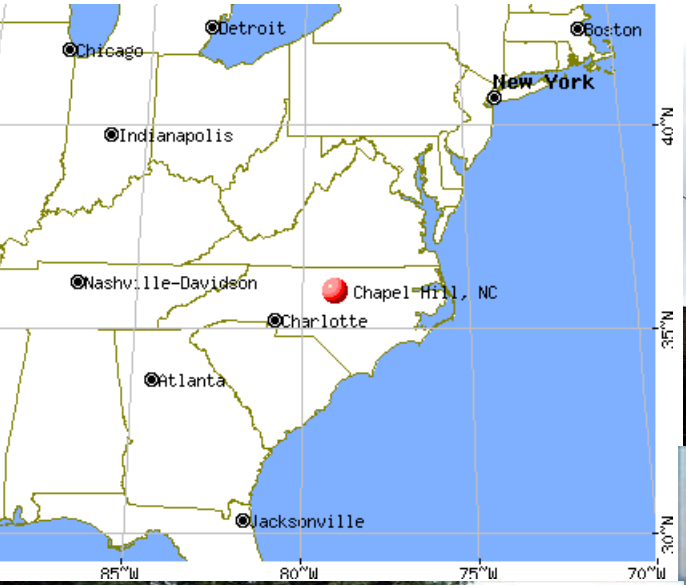


Z. Nie, D. Fava, E. Kumacheva, S. Zou, G. C. Walker and M. Rubinstein, Nature Materials, **6**, 609-614, (2007)

Polymer Self-Assembly

Michael Rubinstein

University of North Carolina at Chapel Hill



What are polymers?

(poly)-(mer) = (many)-(parts) – molecule consisting of many elementary units, called monomers.

Monomers – structural units of a polymer connected to each other by covalent bonds.

N – number of monomers in a polymer is called degree of polymerization.

$M = N M_{mon}$ - mass of a polymer

Examples: synthetic polymer – polyethylene

$CH_3 – CH_2 – CH_2 – CH_2 – CH_2 – \ldots – CH_2 – CH_2 – CH_2 – CH_3$

biological polymer

DNA

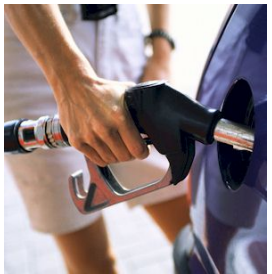
Why Polymers?

Extremely wide range of properties that can be tuned by adjusting primary structure – chemical composition, microstructure, degree of polymerization, and architecture.

E.g. degree of polymerization of alkane hydrocarbons:

$$\ldots -(CH_2 - CH_2)- \ldots$$

# of C atoms	State at 25 °C	Example	Uses
1 – 4	simple gas	propane	gaseous fuels
5 – 15	low viscosity liquid	gasoline	liquid fuels and solvents
16 – 25	viscous liquid	motor oil	oils and greases
20 – 50	simple soft solid	paraffin wax	candles and coatings
> 1000	tough plastic solid	polyethylene	bottles and toys



Homopolymers & Heteropolymers

Homopolymers consist of monomers of only one type:

A – A – A – A – A – A – A – A – A – A – A – A – A – A – A – A

Copolymers - consist of two different monomers

…-A-B-A-B-A-B-A-B-…

alternating

…-A-A-B-A-B-B-B-A-A-B-A-…

random

Block copolymer

…-A-A-B-B-…-B-B-A-A -…-A-A-B-B -…-B-B-A-A -…

Terpolymers – consist of three different monomers

…-A-B-A-C-A-B-C-C-B-A-B-…

Tetrapolymers – consist of four different monomers

… -A-C-D-B-C-A-D-B-C-A-D-A-…

Project for Team AM

Alternating Copolymers

…-A-B-A-B-A-B-A-B-…

…-C-C-C-C-…

How qualitatively different are their physical properties from homopolymers if C = AB is an amphiphilic monomer?

e.g. phase separation, surface tension

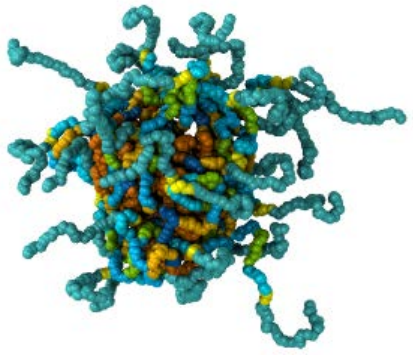
Multi-block Copolymer

…-A-A-B-B-…-B-B-A-A -…-A-A-B-B -…

…-$(A)_k$-$(B)_k$-$(A)_k$-$(B)_k$-$(A)_k$-$(B)_k$-$(A)_k$-$(B)_k$-…

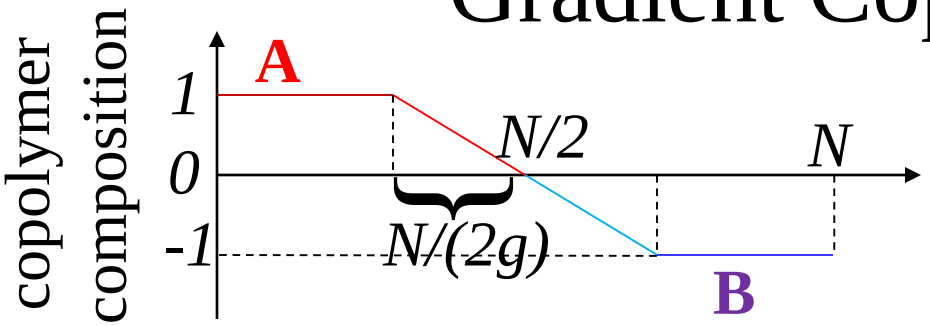
k=1 – alternating,
k=N/2 - diblock

How large does *k* need to be for copolymers to self-assemble into micelles?



Project for Team NZ

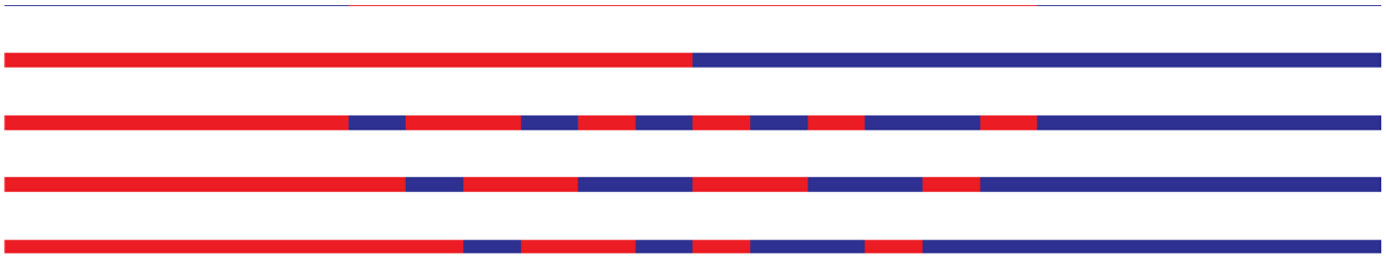
Gradient Copolymers



Gradient $1<g<\infty$

Highest gradient: $g=\infty$ - pure diblock

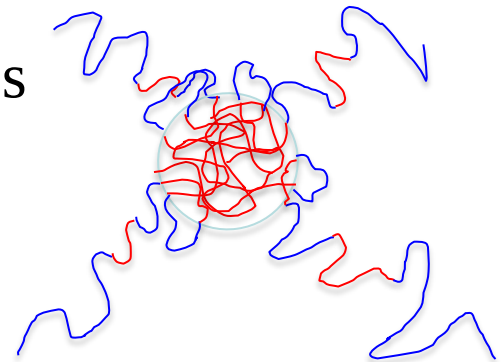
Lowest gradient $g=1$



How does gradient g affects self-assembly of copolymers?

What gradient g results in largest (smallest) micelles (in size and/or in aggregation number)?

What is the internal structure of micelles for $g<\infty$?



Single Chain

Quiz # 1

Who is This Man?

A. Benjamin Franklin

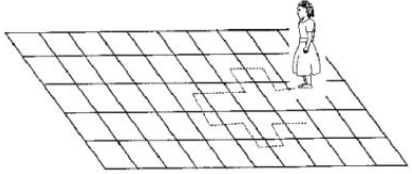
B. Lord William Kelvin

C. Robert Brown

D. Robert Hooke

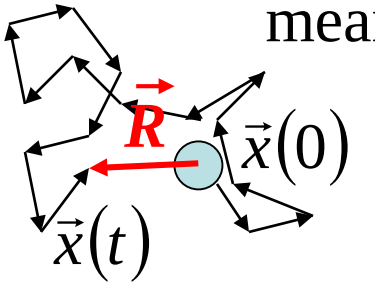
E. None of the above

Random Walk



Why is the trajectory of a diffusing particle similar to a conformation of an ideal chain?

Brownian Diffusion



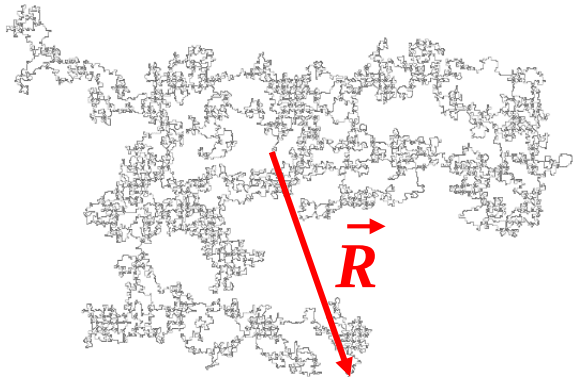
mean-square displacement $\left\langle [\vec{x}(t)-\vec{x}(0)]^2 \right\rangle = 6Dt = b^2 \frac{t}{\tau_0} = b^2 N$

$b^2 = 6D\tau_0$ – mean square step size during time τ_0

$\left\langle \vec{R}^2 \right\rangle = b^2 N$

D – diffusion coefficient

Ideal Polymer



mean-square end-to-end distance $\left\langle \vec{R}^2 \right\rangle = b^2 N$

Polymers are tenuous objects and occupy only a small fraction of their pervaded volume

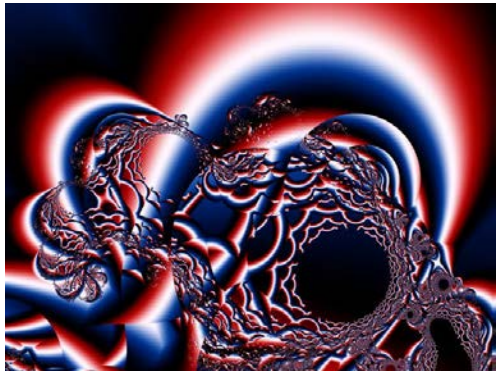
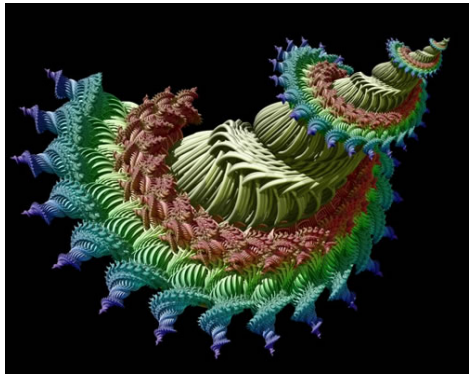
$M \sim R^{d_f}$ - polymers are fractal

Fractal dimension $d_f = 2$ – for polymer melts and some solutions

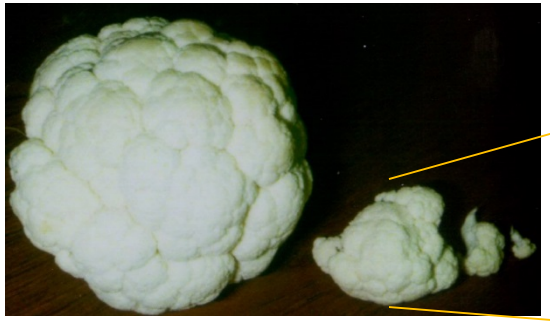
Fractals

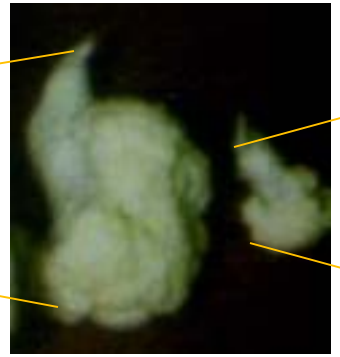
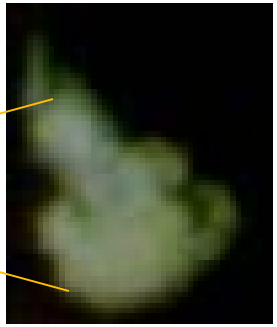
The Art



and Science



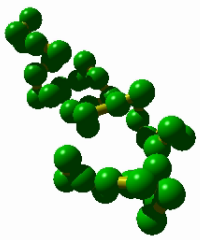
cauliflower

Self-similarity

Magnified part of an object “looks the same” as the whole object.

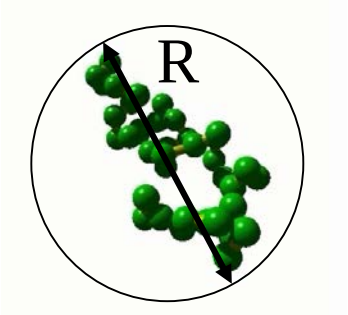
Double Brownian Dance


Robert Brown (1773–1858)



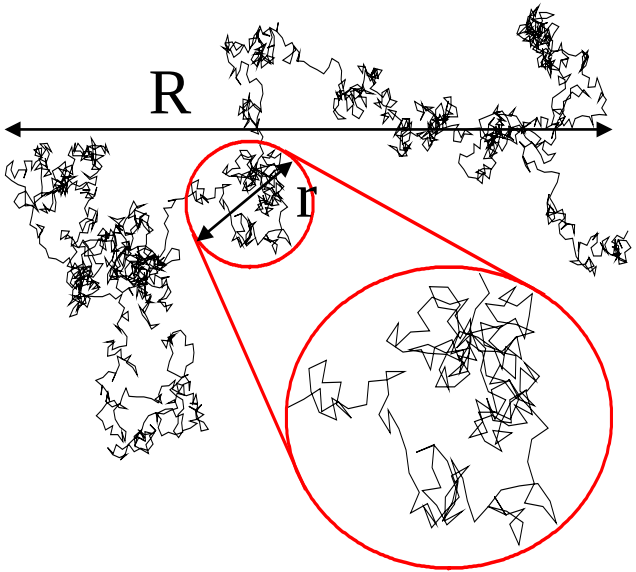
Polymers simultaneously participate in both diffusive motion and conformational rearrangements.

Why are both center of mass trajectory and polymer conformation self-similar (fractal)?



Both are due to thermal motion.

Same physical principles determine their shape on different length scales.



Fractal: magnified small section "looks the same" as the whole polymer

$\langle r^2 \rangle \sim m$ - for a section of a polymer $r \sim m^{\nu}$

Scaling exponent $\nu = 1/d_f = ½$ for melts

$R \sim M^{\nu}$ - for the whole chain

Polymer Length

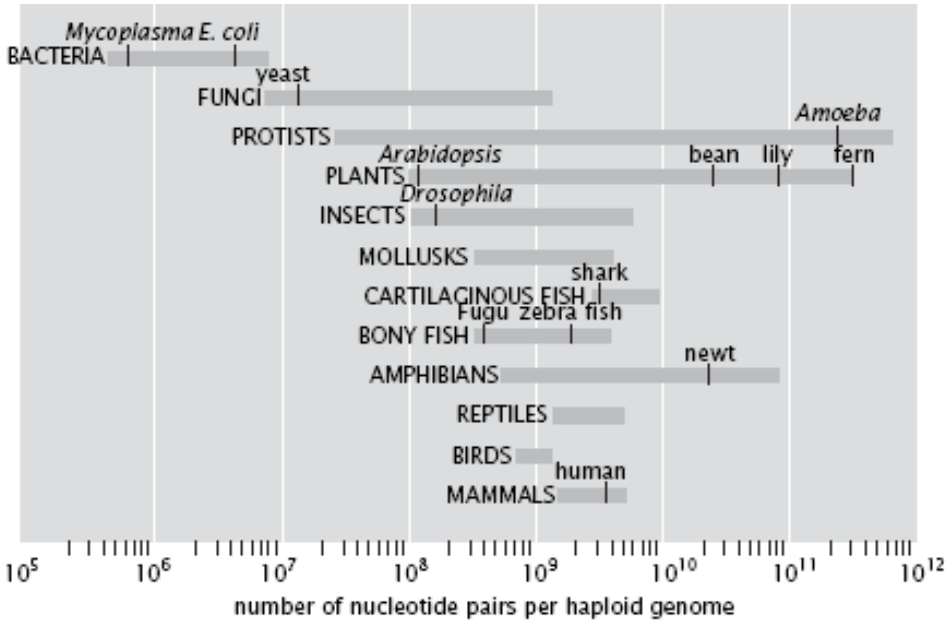
monomer size $b \sim \mathring{A}$

number of monomers

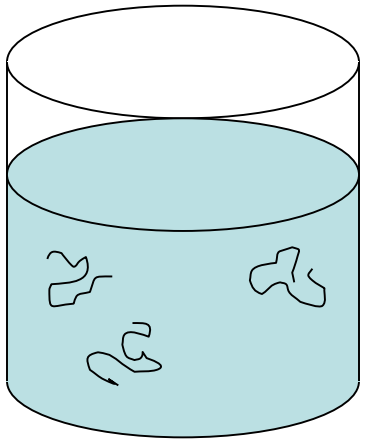
$N \sim 10^2 - 10^{12}$

contour length

$L \sim 10\ nm - 100\ m$



Polymer size depends on intra-molecular interactions and environment



Astronomical Variations of Polymer Size

Increase monomer size by factor of 10^8 $b \sim 1cm.$ Consider $N = 10^{10}$

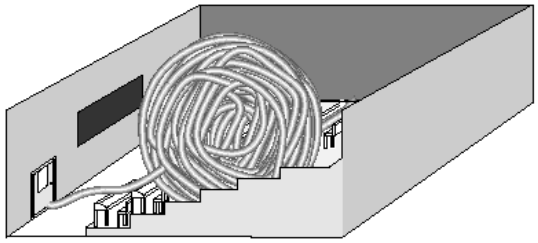
Polymer size depends on intra-molecular interactions (solvent quality).

Poor solvent

$R = bN^{1/3}$

$\sim 20\ m$

globule

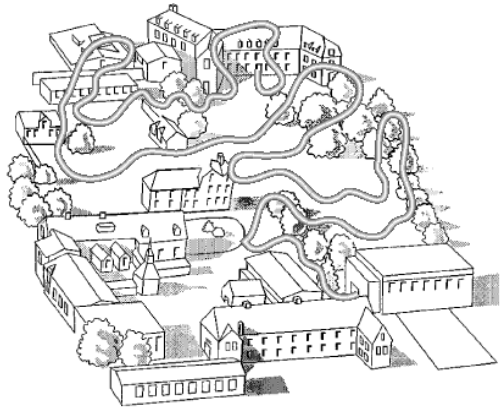


Theta solvent

$R = bN^{1/2}$

$\sim 1\ km$

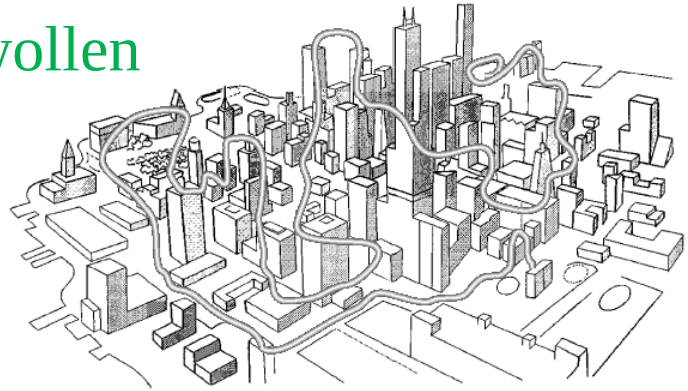
ideal-like



Good solvent

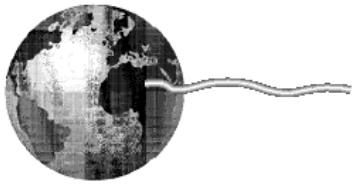
$R = bN^{3/5} \sim 10\ km$

swollen



Long-range repulsion

$R \sim L = bN \sim 10^5\ km$

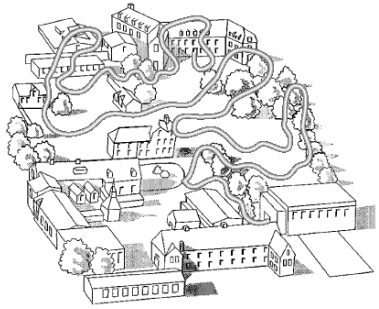


extended

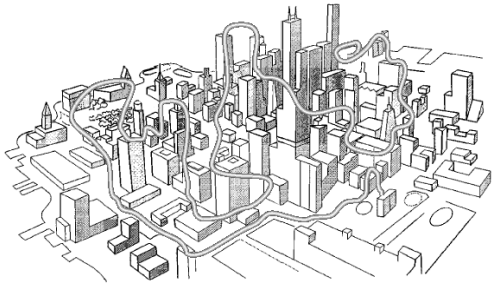
Quiz # 2

Which of These is a Fractal?

A. Ideal-like chains in a theta solvent $R = bN^{1/2}$

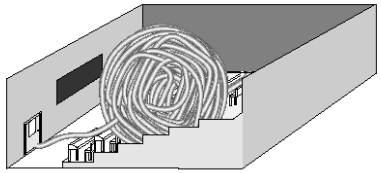


B. Swollen chains in a good solvent



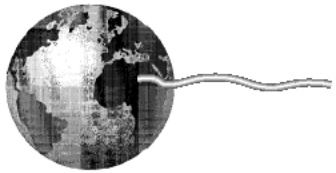
$R = bN^{3/5}$

C. Collapsed polymer in a poor solvent



$R = bN^{1/3}$

D. Strongly extended polymers



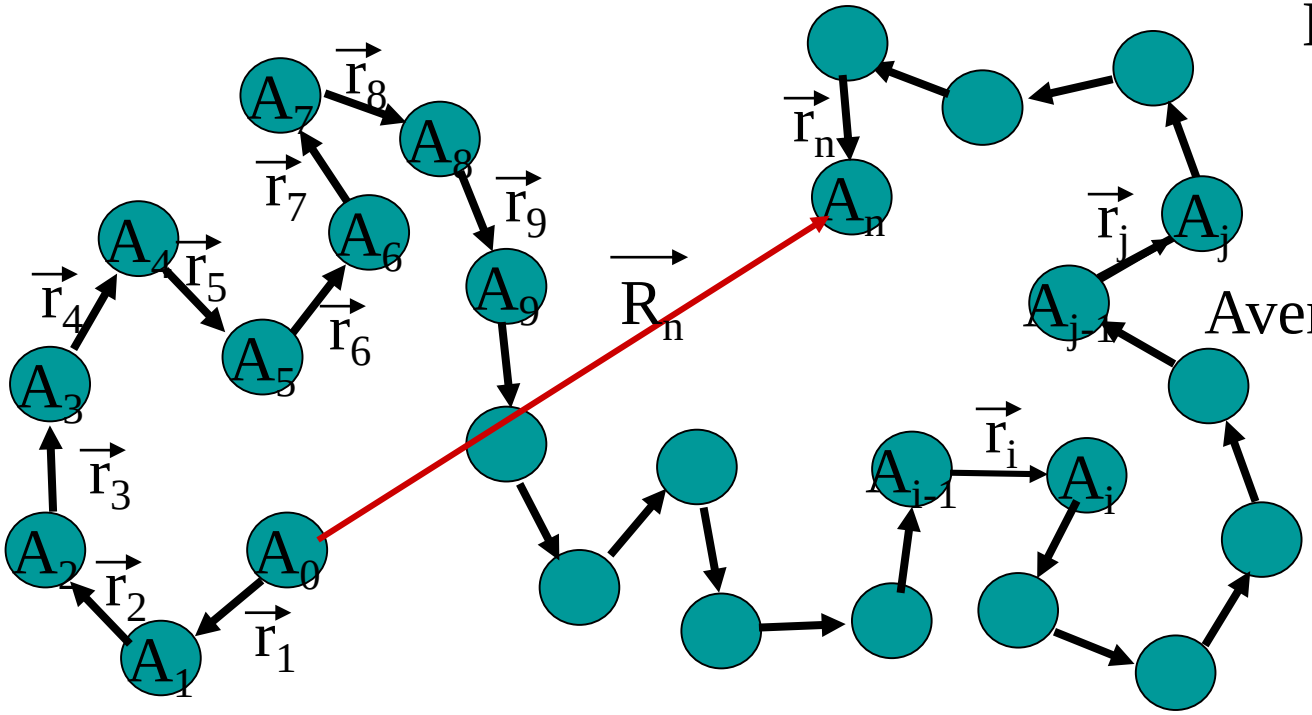
$R \sim L = bN$

Ideal Chains

No interactions between monomers that are far along the chain, even if they approach each other in space.

Ideal chains are good models for polymer melts, concentrated solutions, and solutions at θ-temperature.

$\vec{r}_i$ - bond vector between backbone atoms A_{i-1} and A_i



End-to-end vector

$$\vec{R}_N = \sum_{i=1}^{N} \vec{r}_i$$

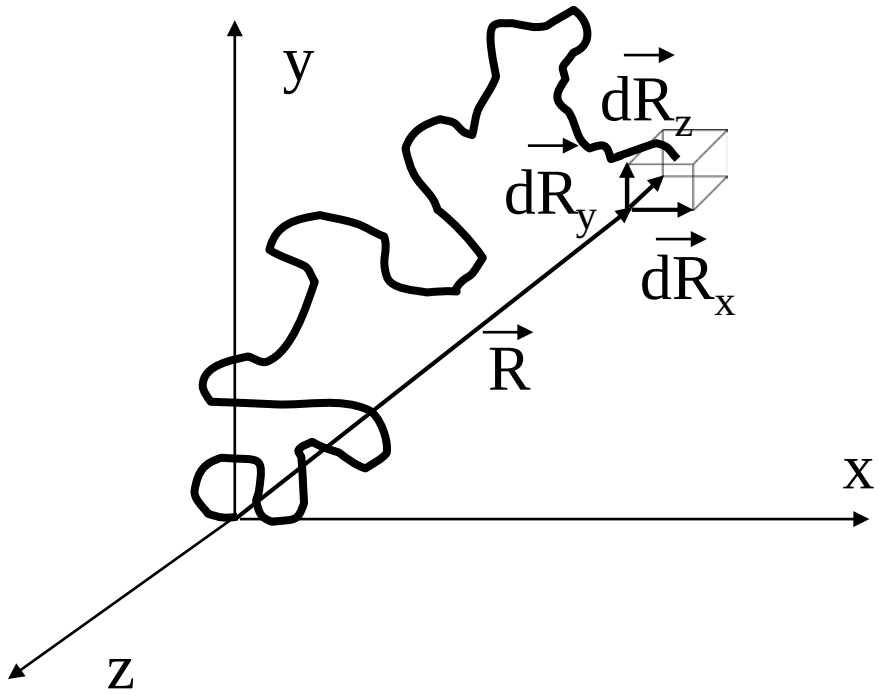
Average end-to-end vector

$$\left\langle \vec{R}_N \right\rangle = 0$$

$\langle ... \rangle$- ensemble average

$$\left\langle R^2 \right\rangle = Nb^2$$

Distribution of End-to-End Vectors



Probability for an *N*-step walk with step size b to start at the origin and to end within volume $dR_x dR_y dR_z$ of the point with displacement vector $\vec{R}$ is

$$P_{3d}\left(N,\vec{R}\right)=\left(\frac{3}{2\pi Nb^2}\right)^{3/2}\exp\left(-\frac{3R^2}{2Nb^2}\right)$$

$$\left\langle R^2\right\rangle = Nb^2$$

Quiz # 3

Who is This Man?

A. Carl Friedrich Gauss

B. Ludwig Boltzmann

C. Lord William Kelvin

D. Robert Hooke

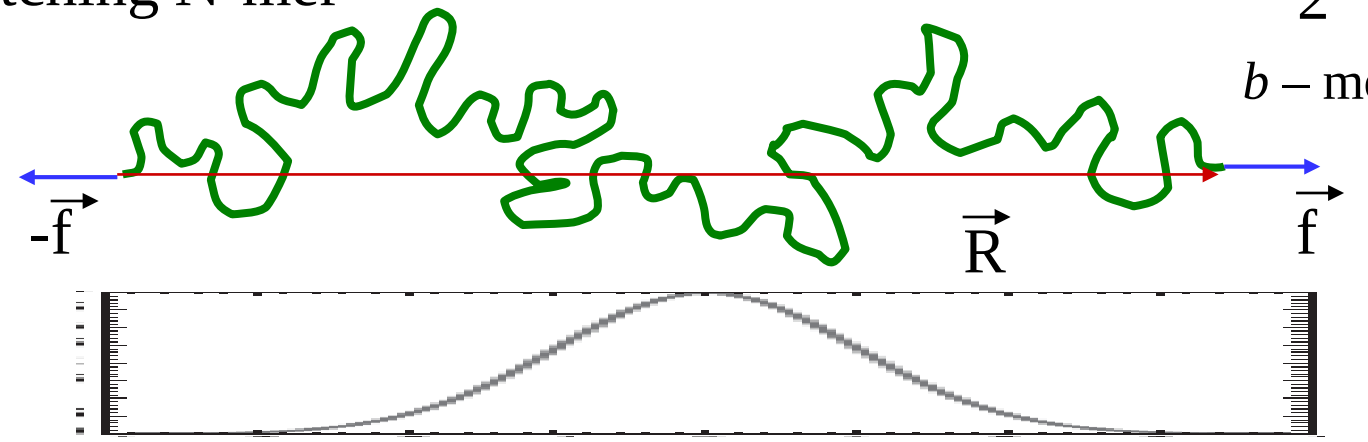
E. None of the above

Entropic Elasticity

Entropic free energy cost for stretching N-mer

$$F\left(N,\vec{R}\right) = -kT \ln P_{3d}\left(N,\vec{R}\right) = \frac{3}{2} kT \frac{\vec{R}^2}{Nb^2}$$

b – monomer size



Number of chain conformations decreases with end-to-end vector, leading to decreasing polymer entropy and increasing free energy.

To hold a chain at a given end-to-end vector requires a pair of equal and opposite forces acting at chain ends

$$f_x = \frac{\partial F\left(N,\vec{R}\right)}{\partial R_x} = \frac{3kT}{Nb^2} R_x$$

Hooke's Law $\vec{f} = \frac{3kT}{Nb^2}\vec{R}$ with entropic spring constant $\frac{3kT}{Nb^2}$

e.g. rubber band

THE FAR SIDE By GARY LARSON

On Oct. 23, 1927, three days after its invention, the first rubber band is tested.

Summary of Ideal Chains

Ideal chains: no interactions between monomers separated by many bonds

Mean square end-to-end distance of ideal linear polymer $\left\langle R^2 \right\rangle = Nb^2$

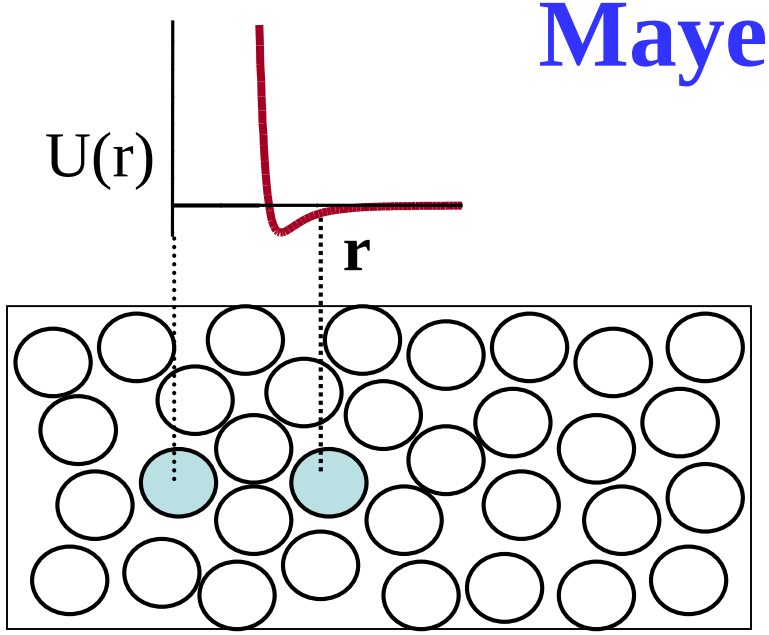
Probability distribution function $P_{3d}\left(N,\vec{R}\right)=\left(\frac{3}{2\pi Nb^2}\right)^{3/2}\exp\left(-\frac{3R^2}{2Nb^2}\right)$

Free energy of an ideal chain $F=\frac{3}{2}kT\frac{\vec{R}^2}{Nb^2}$

Entropic Hooke's Law $\vec{f}=\frac{3kT}{Nb^2}\vec{R}$

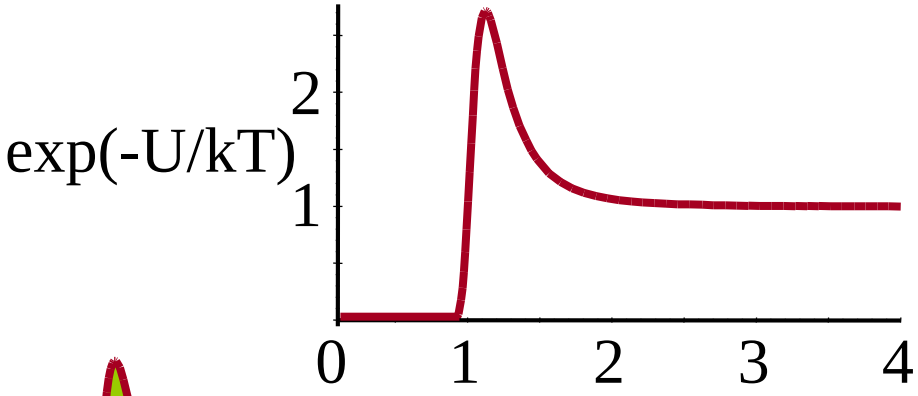
Real Chains: Monomer Interactions

Mayer f-function



Effective interactions potential between two monomers in a solution of other molecules.

Relative probability of finding two monomers at distance r

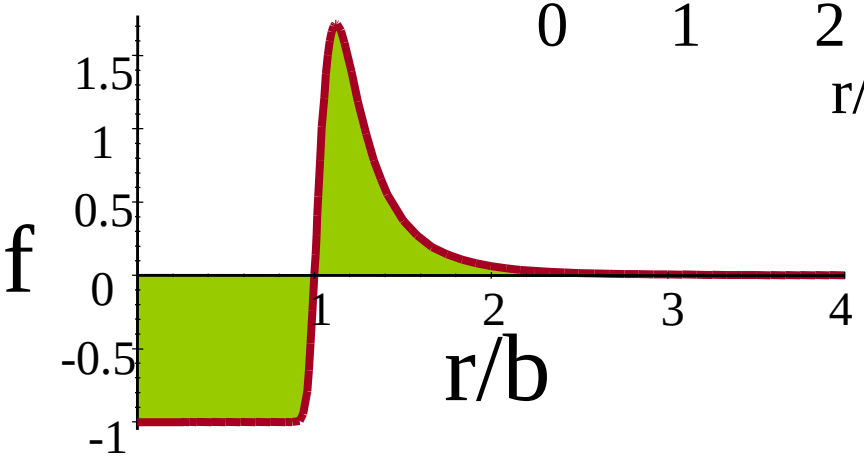


Mayer f-function

$$f(r) = \exp\left[-\frac{U(r)}{kT}\right] - 1$$

Excluded volume

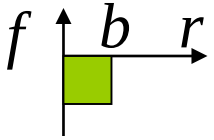
$$v = -\int f(\vec{r})\, d^3 r$$



Classification of Solvents

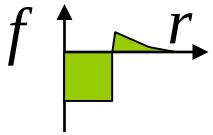
$$\mathrm{v} = -\int f(\vec{r})\, d^3 r \qquad f(r) = \exp\left[-\frac{U(r)}{kT}\right] - 1$$

Athermal solvents high T limit



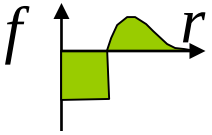
$\mathrm{v} \approx b^3$

Good solvents repulsion dominates



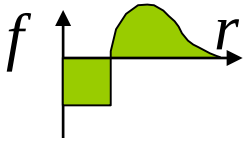
$0 < \mathrm{v} < b^3$

Theta solvents attraction balances repulsion



$\mathrm{v} = 0$

Poor solvents attraction dominates



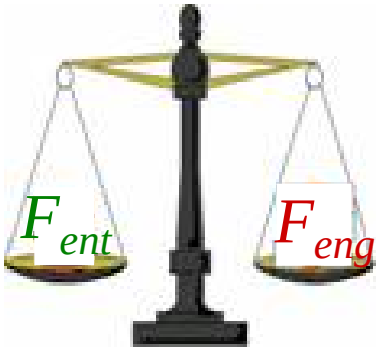
$\mathrm{v} < 0$

Typically repulsion dominates at higher temperatures while attraction dominates at lower temperatures.

Life of a Polymer is a Balance

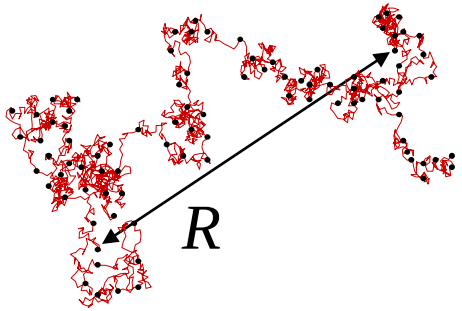
of entropic and energetic parts of free energy

Entropic part "wants" chains to have ideal-like conformations



Energetic part typically "wants" something else (e.g. fewer monomer-monomer contacts in a good solvent).

Chain has to find a compromise between these two desires and optimize its shape and size.



Flory Theory

Number density of monomers in a chain is N/R^3

Probability of another monomer being within excluded volume v of a given monomer is vN/R^3

Excluded volume interaction energy per monomer $kTvN/R^3$

Excluded volume interaction energy per chain $kTvN^2/R^3$

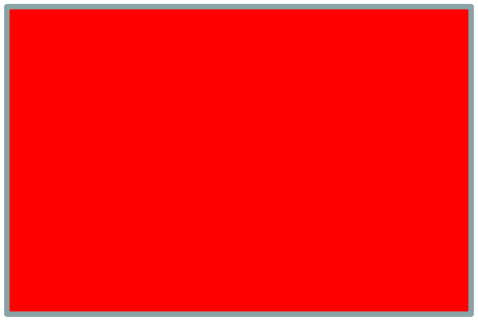
Entropic part of the free energy is on order $kTR^2/(Nb^2)$

Flory approximation of the total free energy of a real chain

$$F \approx kT\left(v\frac{N^2}{R^3}+\frac{R^2}{Nb^2}\right)$$

$$R^5 \approx vb^2N^3$$

chain in good solvent



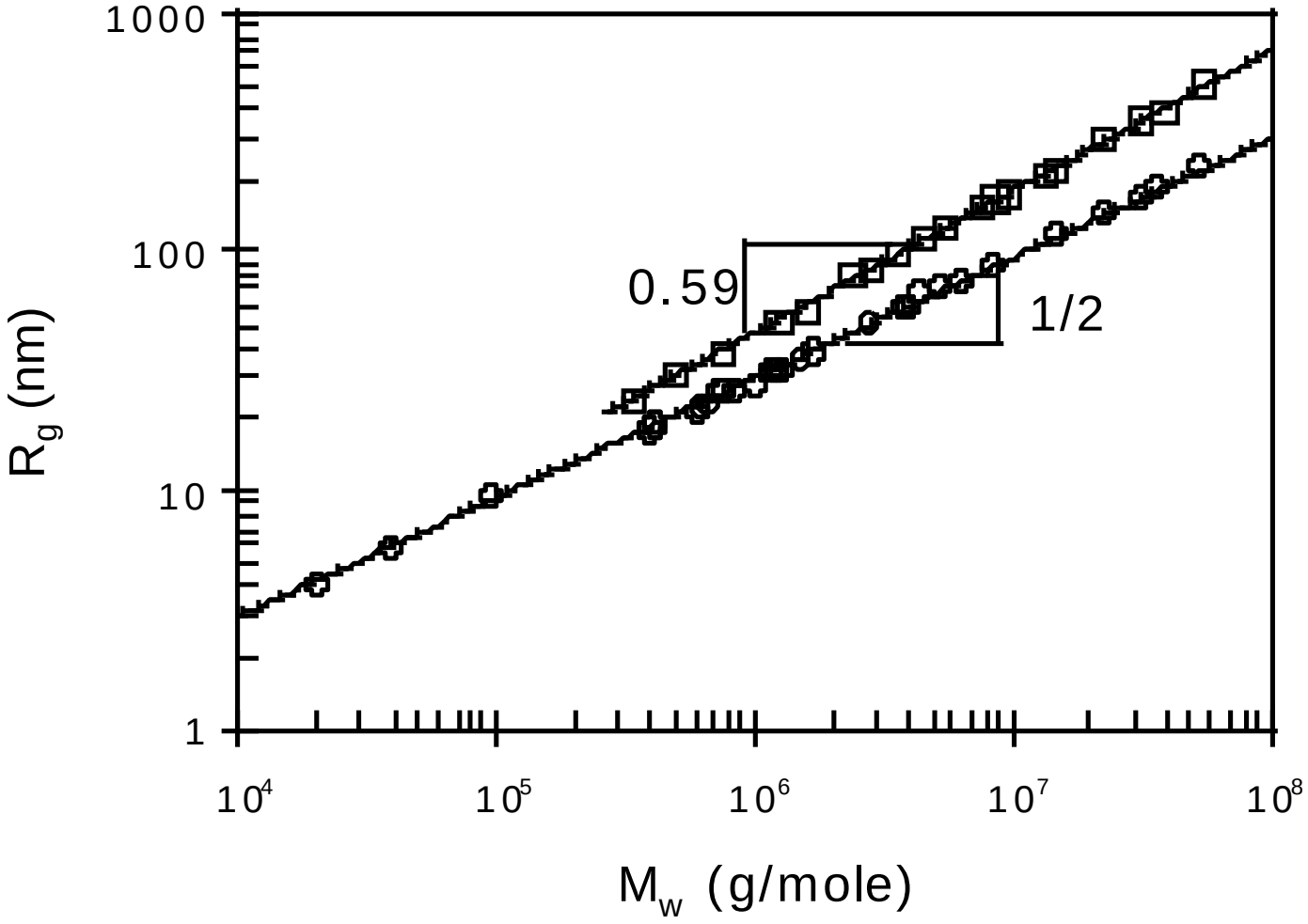
Free energy is minimum at $R \approx v^{1/5}b^{2/5}N^{3/5}$

Universal relation $R \sim N^{\nu}$

Flory scaling exponent $\nu = 3/5$

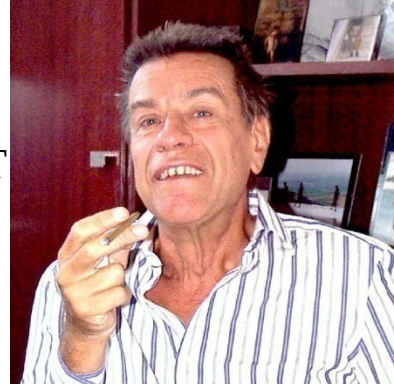
More accurate estimate $\nu \cong 0.588$

Size of Polystyrene in Different Solvents

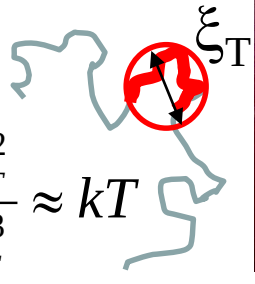


Polystyrene in a θ-solvent (cyclohexane at 34.5°C)
and in a good solvent (benzene at 25°C).
Fetters et al *J. Phys. Chem. Ref. Data* **23**, 619 (1994)

Scaling Model of Real Chains



Thermal blob - length scale at which excluded volume interactions are of order kT



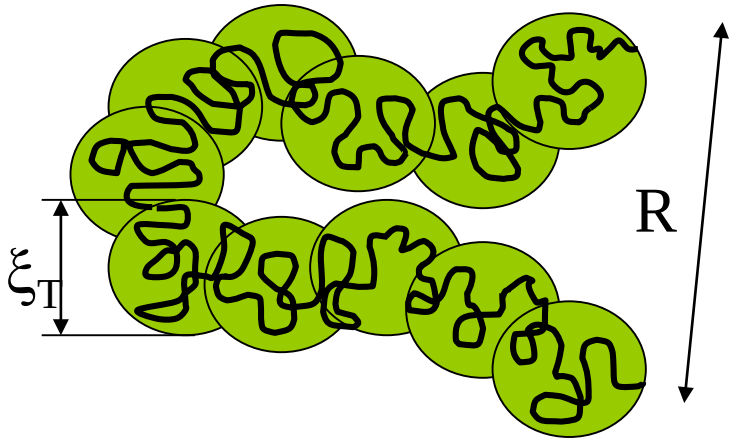
$$kT|\mathrm{v}|\frac{g_T^2}{\xi_T^3} \approx kT$$

Chain is ideal on length scales smaller than thermal blob $\xi_T \approx b g_T^{1/2}$

Number of monomers in a thermal blob $g_T \approx b^6/\mathrm{v}^2$

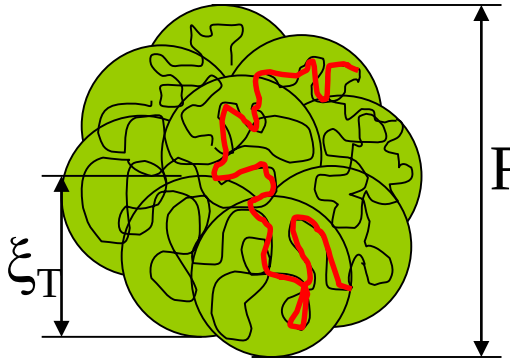
Size of a thermal blob $\xi_T \approx \frac{b^4}{|\mathrm{v}|}$

good solvent v>*0*



$$R \approx \xi_T \left(\frac{N}{g_T}\right)^{3/5} \approx b\left(\frac{\mathrm{v}}{b^3}\right)^{1/5} N^{3/5}$$

poor solvent v<*0*



Chain strands of $g_{conf} \sim (R_{gl}/b)^2$ are almost ideal

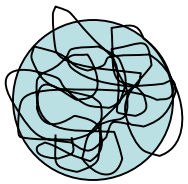
$$R \approx \xi_T \left(\frac{N}{g_T}\right)^{1/3} \approx \frac{b^2}{|\mathrm{v}|^{1/3}} N^{1/3}$$

Flory Theory of a Polymer in a Poor Solvent

$$F \approx kT\left(\mathrm{v}\frac{N^2}{R^3}+\frac{R^2}{Nb^2}\right)$$

In poor solvent $\mathrm{v} < 0$ and $R \to 0$

Cost of Confinement



$R < Nb^2$

Confinement blob of size R with g_{conf} monomers

$$g_{conf} \approx \left(\frac{R}{b}\right)^2$$

Confinement free energy $F_{conf} \approx kT\dfrac{N}{g_{conf}} \approx kT\dfrac{Nb^2}{R^2}$

$$F \approx kT\left(\mathrm{v}\frac{N^2}{R^3}+\frac{R^2}{Nb^2}+\frac{Nb^2}{R^2}\right)$$

For $\mathrm{v} < 0$ $R \to 0$

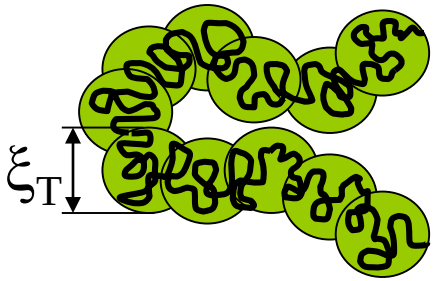
Three Body Repulsion

$$F \approx kT\left(\frac{R^2}{Nb^2}+\frac{Nb^2}{R^2}+\mathrm{v}\frac{N^2}{R^3}+w\frac{N^3}{R^6}\right)$$

Size of a globule

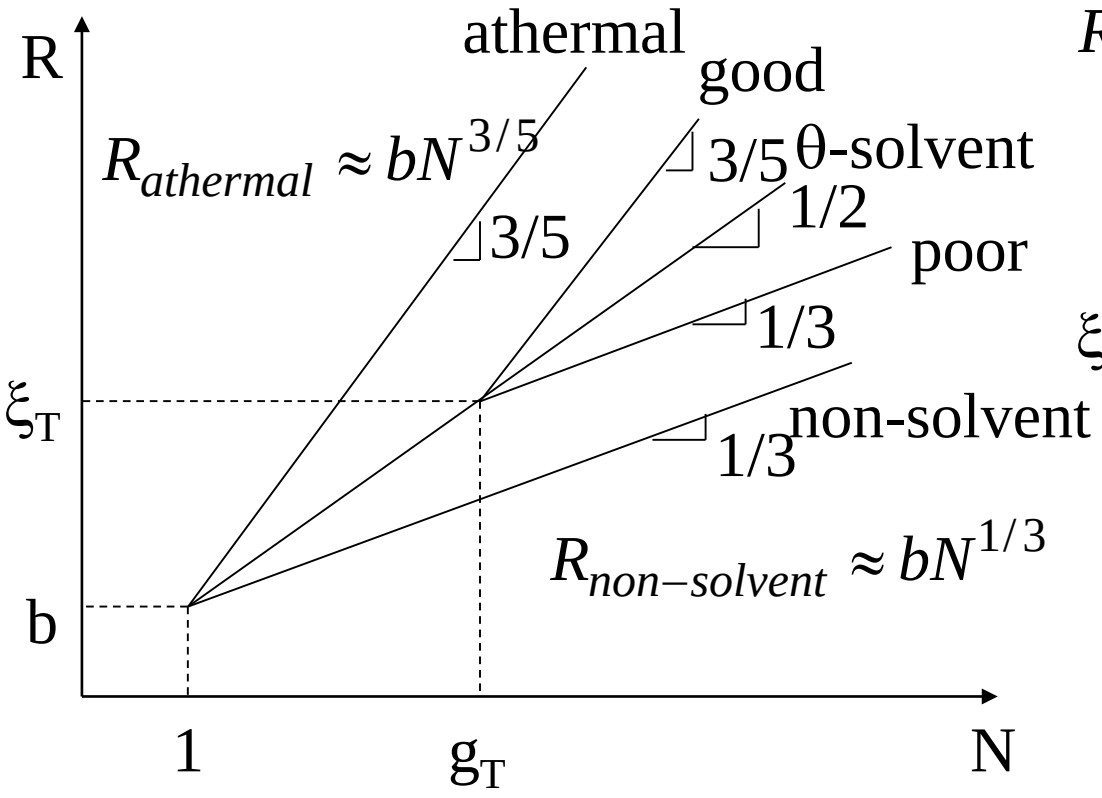
$$R_{gl} \approx \left(\frac{wN}{|\mathrm{v}|}\right)^{1/3}$$

Size of Polymers in Different Solvents

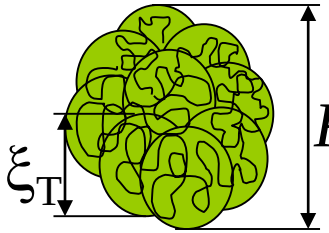


$R_{good} \approx \xi_T \left(\frac{N}{g_T} \right)^{3/5}$ swollen in good solvents

log – log plot



$R_\theta \approx bN^{1/2}$ nearly ideal in θ-solvents



$R_{poor} \approx \xi_T \left(\frac{N}{g_T} \right)^{1/3}$

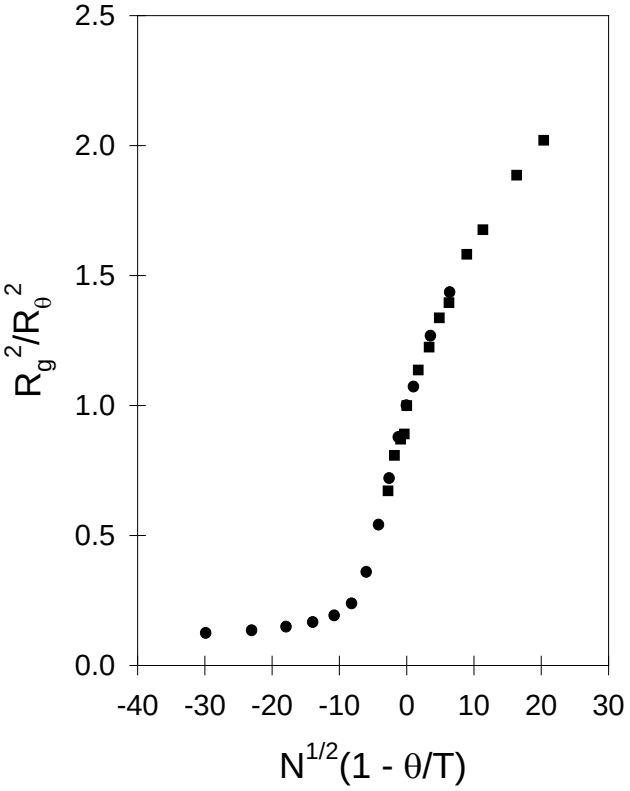
collapsed into a globule in poor solvents

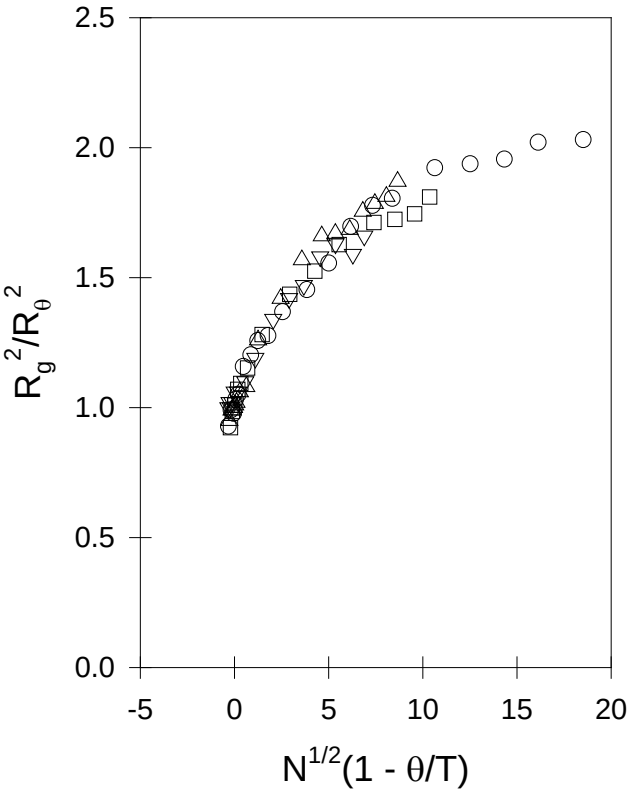
T-dependence of v (UCST)

$$v \approx \left(1 - \frac{\theta}{T}\right) b^3$$

Chain size variation wrt ideal depends on interaction parameter $z \sim (N/g_T)^{1/2} \sim (v/b^3)N^{1/2}$

Temperature Dependence of Chain Size





Monte-Carlo simulations
Graessley et.al., Macromolecules **32**, 3510, 1999 & I. Withers

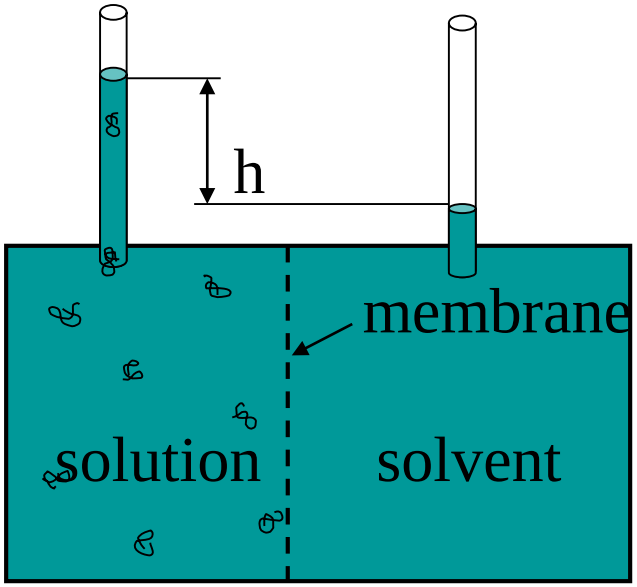
Polystyrene in decalin
Berry, J. Chem. Phys. **44**, 4550, 1966

$$v \approx \left(1 - \frac{\theta}{T}\right) b^3$$

interaction parameter $z \sim (N/g_T)^{1/2} \sim N^{1/2}(v/b^3) \sim N^{1/2}(1-\theta/T)$

Many Chains

Intermolecular Interactions



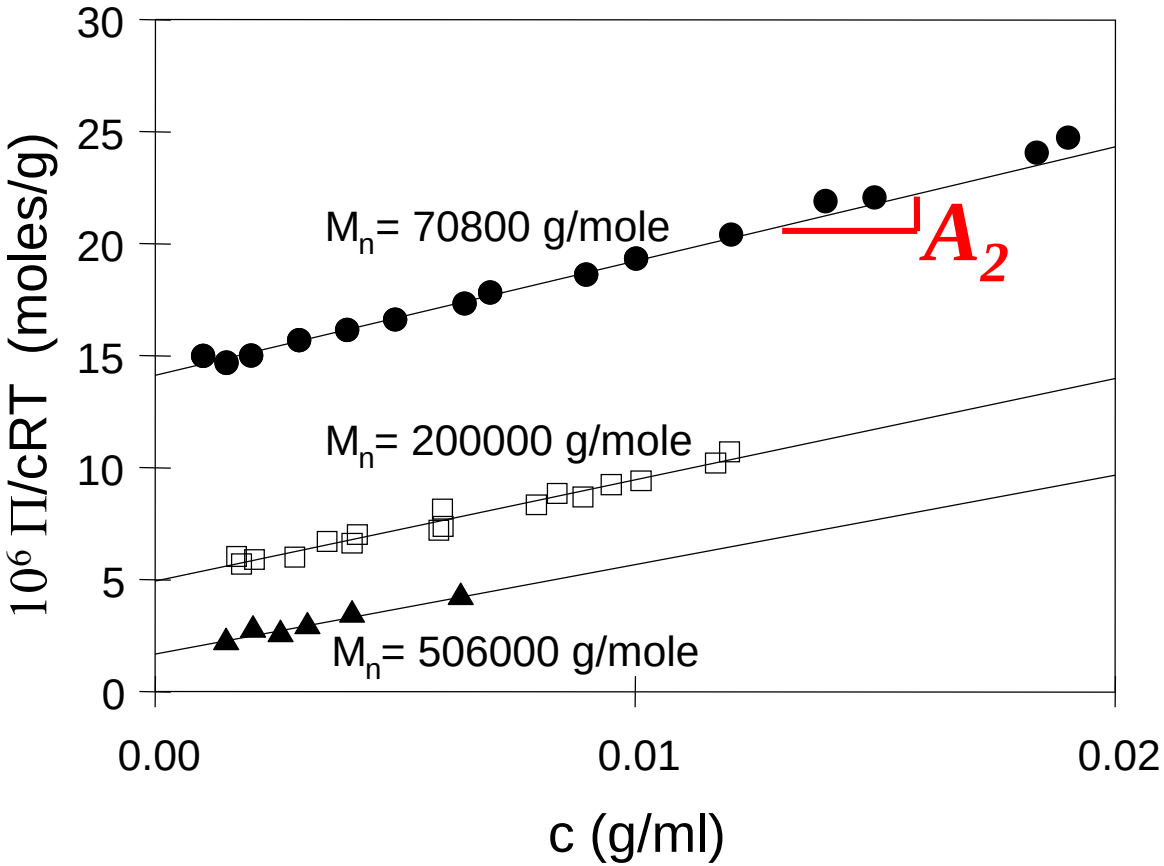
Osmometer

Poly(α-methylstyrene) in toluene at 25 °C
Noda et al, Macromol. **16**, 668, 1981

Osmotic pressure

$$\Pi = RT\left(\frac{c}{M_n} + A_2 c^2 + \ldots\right)$$

A_2 – second virial coefficient



Second Virial Coefficient

Near θ-temperature chains are smaller than thermal blobs and easily interpenetrate each with monomers directly interacting with each other. Second virial coefficient is proportional to excluded volume

$$A_2 \approx \frac{N_{Av}}{M_0^2}\mathrm{v} \approx \frac{N_{Av}b^3}{M_0^{3/2}}\frac{z}{M^{1/2}} \qquad \text{for} \qquad |z|<1$$

interaction parameter $z \sim (N/g_T)^{1/2} \sim (\mathrm{v}/b^3)N^{1/2}$

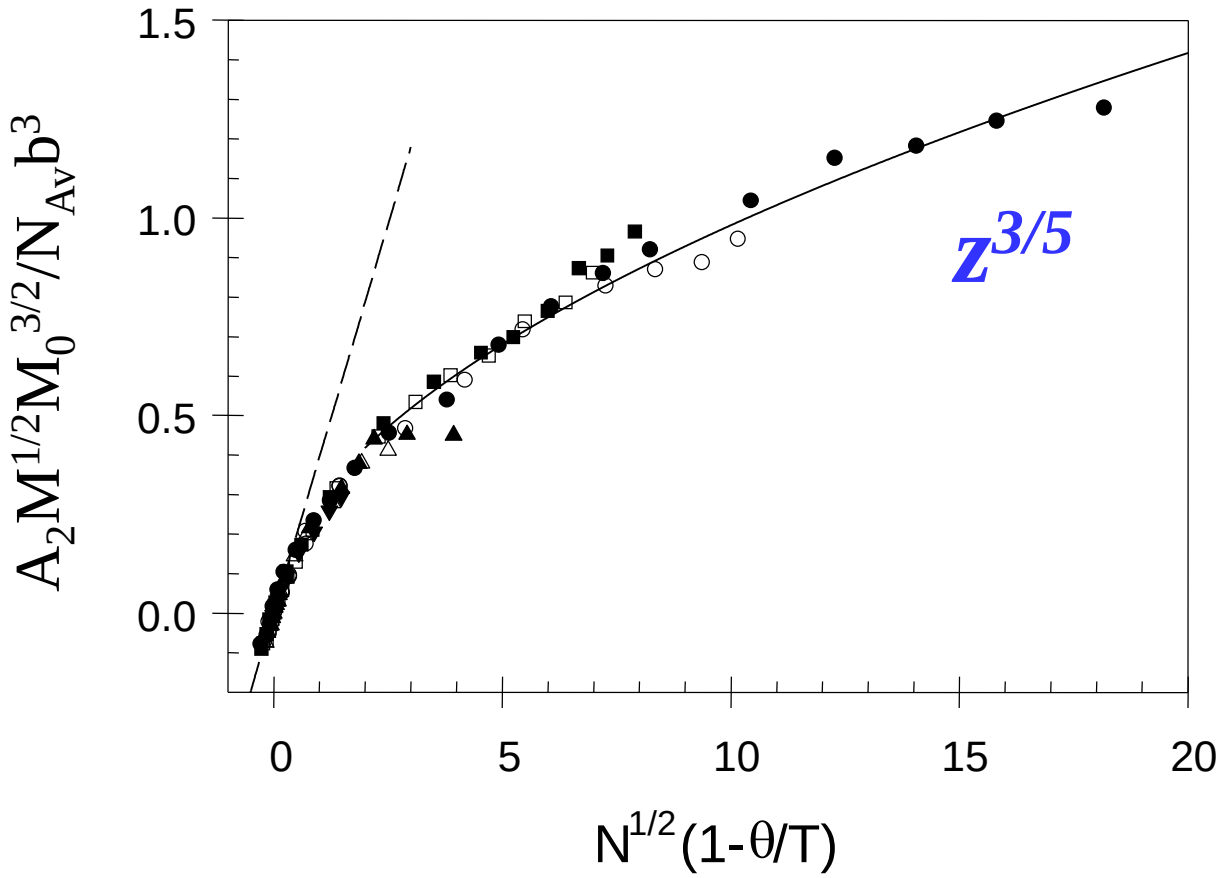
In good solvents chains repel each other strongly and do not interpenetrate. Second virial coefficient of chains is proportional to their volume.

$$A_2 \approx \frac{N_{Av}}{M^2}R^3 \approx \frac{N_{Av}b^3}{M_0^{3/2}}\frac{z^{6\nu-3}}{M^{1/2}} \qquad \text{for} \qquad z>1$$

Universal function

$$\frac{A_2 M^{1/2} M_0^{3/2}}{N_{Av}b^3} = f(z) \approx \begin{cases} z & \text{for } |z|<1 \\ z^{6\nu-3} & \text{for } z>1 \end{cases}$$

Second Virial Coefficient Universal Plot



Polystyrene in decalin
G. C. Berry, J. Chem. Phys. **44**, 4550, 1966

interaction parameter $z \sim (N/g_T)^{1/2} \sim N^{1/2}(v/b^3) \sim N^{1/2}(1-\theta/T)$

Polymer Melts

Consider a blend with a small concentration of N_A chains in a melt of chemically identical N_B chains.

No energetic contribution to conformations of A in B

Excluded volume due to translational entropy of mixing B molecules with A chain $\mathrm{v} = \frac{b^3}{N_B}$ is very small for $N_B >> 1$

Thermal blob $g_T \approx \frac{b^6}{\mathrm{v}^2} = N_B^2$ $\xi_T \approx b\sqrt{g_T} \approx bN_B$

Chains smaller than thermal blob $N_A < N_B^2$ are nearly ideal.

In monodisperse $N_A = N_B$ and weakly polydisperse melts chains are almost ideal.

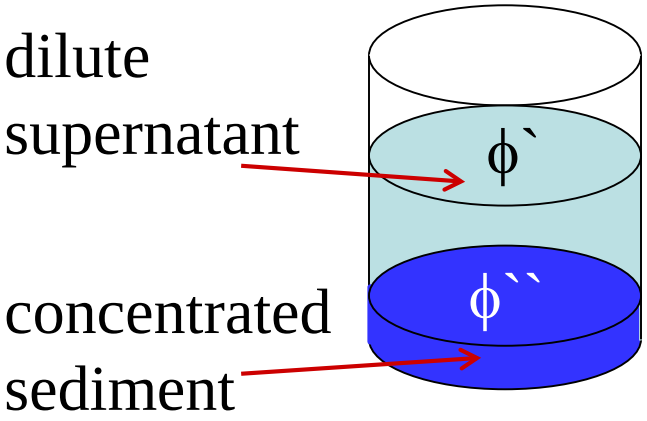
Flory theorem

Phase Diagram of Polymer Solutions

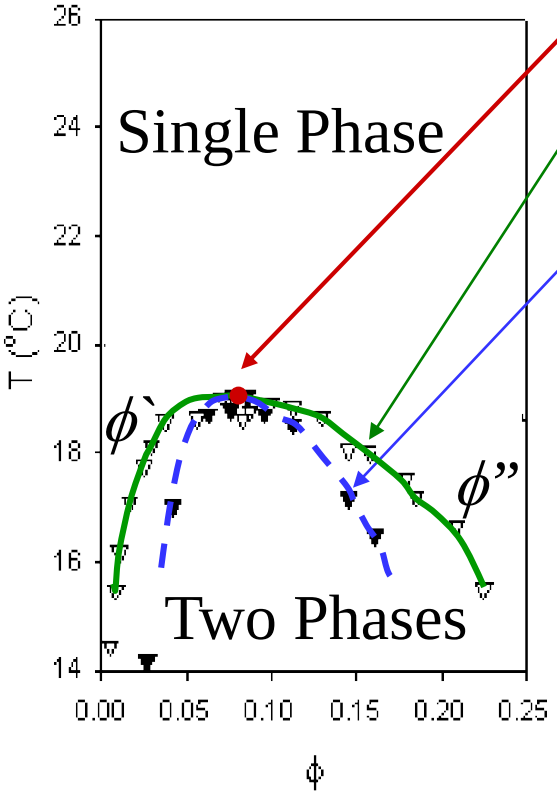
Polymer solutions phase separate upon decreasing solvent quality below θ-temperature

Upper Critical Solution Temperature (UCST)

Solution phase separates below the binodal in poor solvent regime into a dilute supernatant of isolated globules at ϕ` and concentrated sediment at ϕ``.



dense packing of thermal blobs



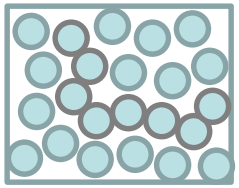
M=53.3kg/mole

Polyisoprene in dioxane
Takano et al., Polym J. 17, 1123, 1985

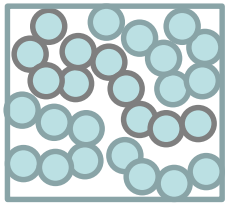
Quiz # 4

Which of These Chains are Ideal?

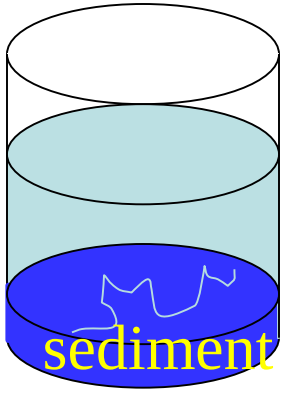
A. Polymer in a solution of its monomers



B. Polymer dissolved in a melt of identical chains

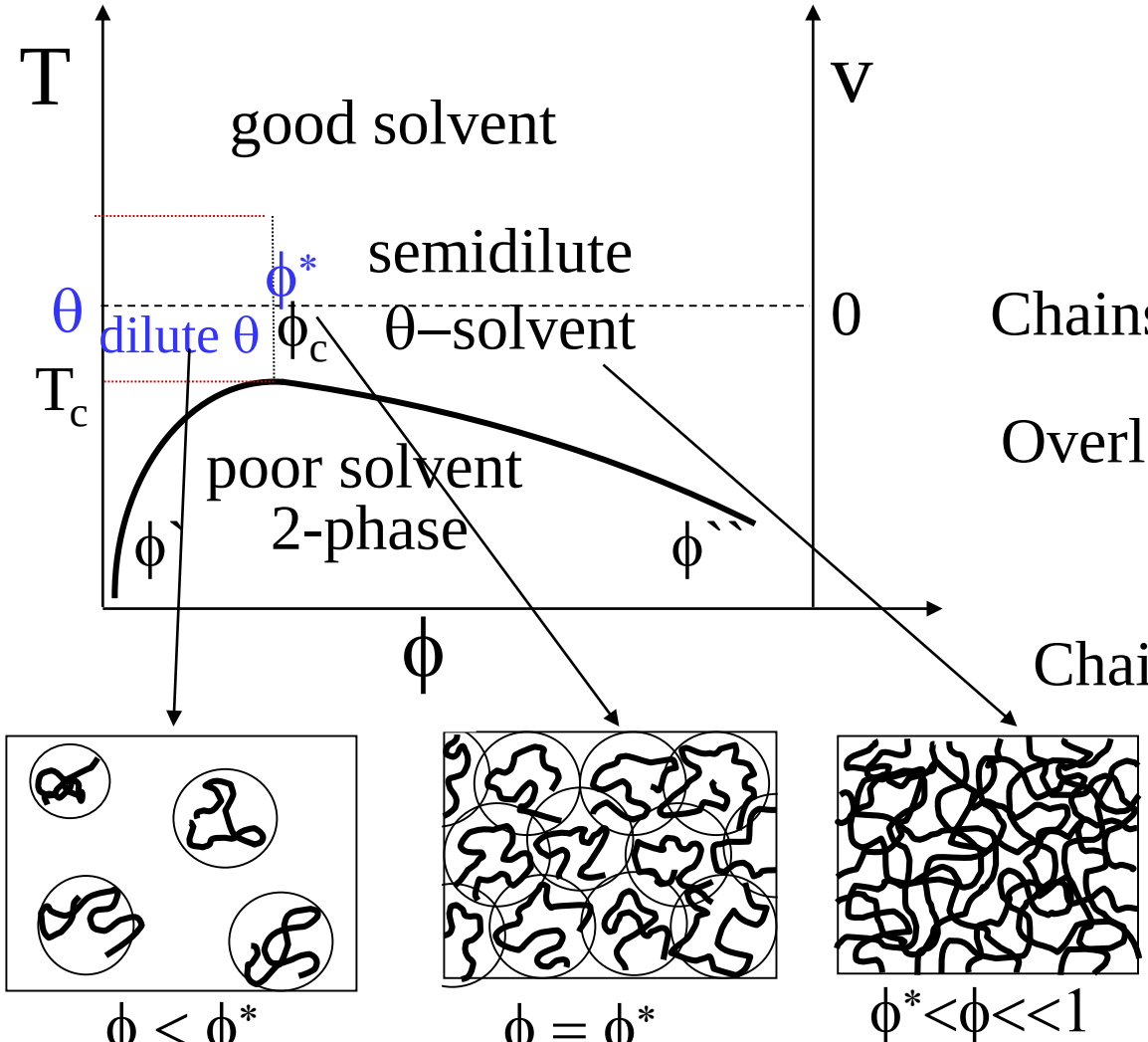


C. Chain in a sediment in a poor solvent



D. None of the above

Polymer Solutions



Theta solvent

$$\mathrm{v} = \frac{T-\theta}{T} b^3 = 0$$

Chains are nearly ideal $R = b\sqrt{N}$

Overlap concentration

$$\phi_\theta^* \approx \frac{Nb^3}{R^3} = \frac{1}{\sqrt{N}}$$

Chain is ideal if it is smaller than thermal blob $\xi_T \approx \frac{b^4}{|\mathrm{v}|}$

Boundaries of dilute θ-regime

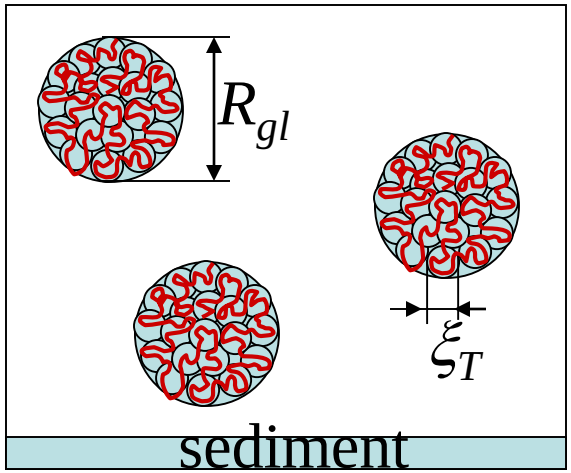
$$|\mathrm{v}| = \left|\frac{T-\theta}{T}\right| b^3 = \frac{b^3}{\sqrt{N}}$$

Temperatures at which chains begin to either swell or collapse

$$T \approx \theta\left(1 \pm \frac{1}{\sqrt{N}}\right)$$

Poor Solvent

Dilute Supernatant of Globules



Globules behave as liquid droplets with size

$$R_{gl} \approx \frac{b^2 N^{1/3}}{|\mathrm{v}|^{1/3}} \qquad \xi_T \approx \frac{b^4}{|\mathrm{v}|}$$

Surface tension is of order kT per thermal blob

$$\gamma \approx \frac{kT}{\xi_T^2} \approx \frac{kT}{b^8}\mathrm{v}^2$$

Total surface energy of a globule

$$\gamma R_{gl}^2 \approx \frac{kTR_{gl}^2}{\xi_T^2} \approx \frac{kT|\mathrm{v}|^{4/3}}{b^4} N^{2/3}$$

is balanced by its translational entropy $kT\ln\phi$'

Concentration of a dilute supernatant

$$\phi' = \phi'' \exp\left(-\frac{\gamma R_{gl}^2}{kT}\right) \approx \frac{|\mathrm{v}|}{b^3} \exp\left(-\frac{|\mathrm{v}|^{4/3}}{b^4} N^{2/3}\right)$$

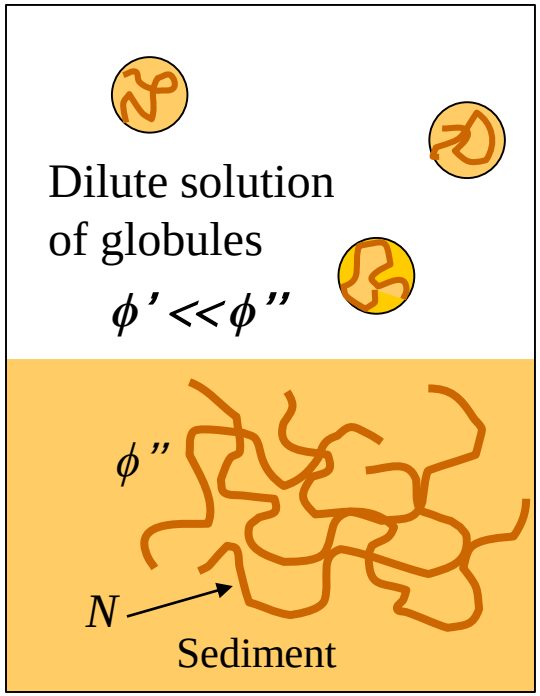
is different from the mean field prediction.

Quiz #5

Why are we ignoring hydrophobic energy of globular cores?

Surface Tension γ

hydrophobic homopolymer B
in two phase solution



ϕ' - volume fraction of hydrophobic B chains in dilute phase of globules

ϕ'' - volume fraction of sediment (and inside micelles)

Equilibrium between phases $\mu' = \mu''$

Chemical potential of a chain in sediment

$$\mu'' = kT\ln(\phi''/N) + F_0$$

Chemical potential of a globule

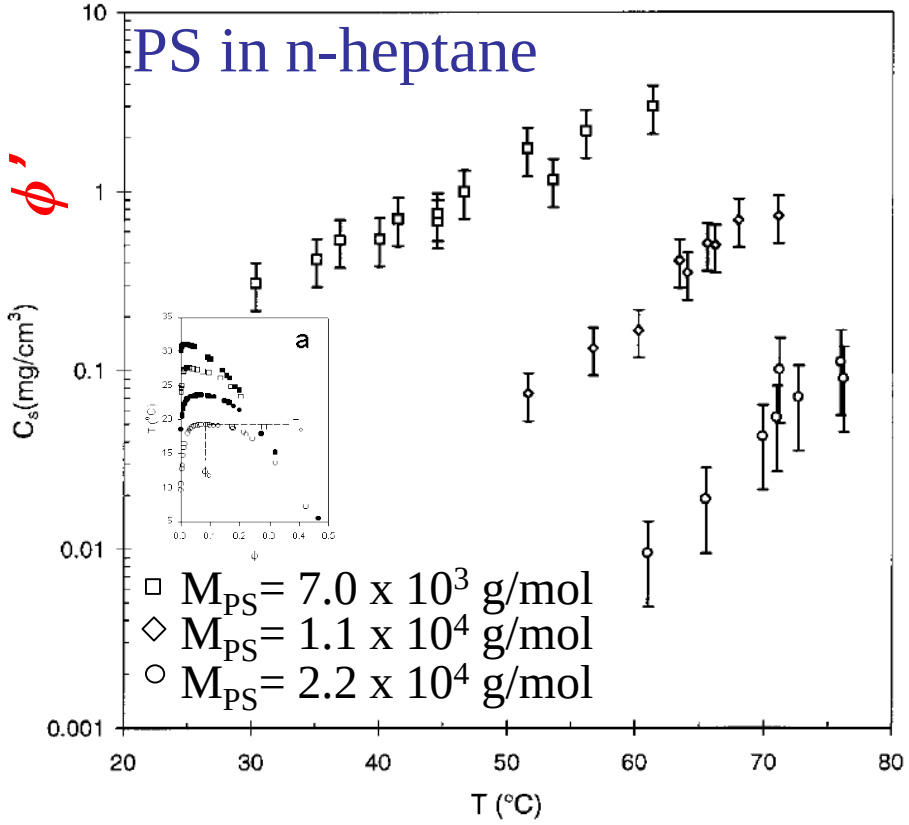
$$\mu' = kT\ln(\phi'/N) + F_0 + F_{interface}$$

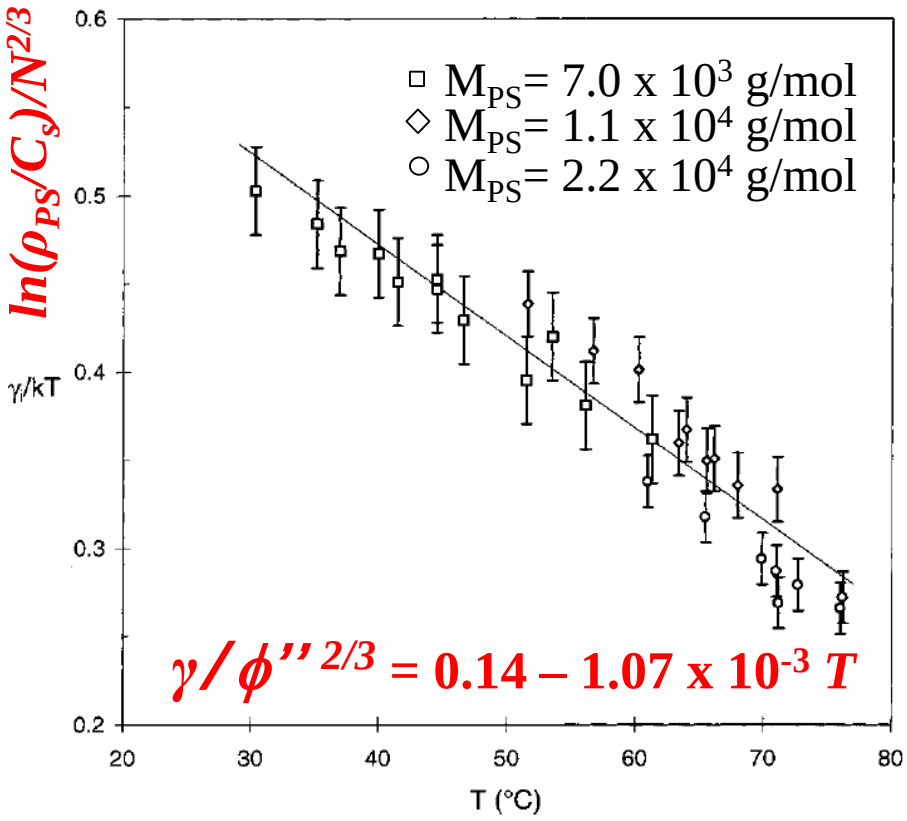
$$F_{interface} = 4\pi R^2\gamma \approx \gamma(N/\phi'')^{2/3}$$

$$\ln(\phi''/\phi') \approx \gamma(N/\phi'')^{2/3}/kT$$

Determine surface tension γ from temperature dependence of volume fraction ϕ' of dilute globules.

Surface Tension from Concentration of Dilute Globules





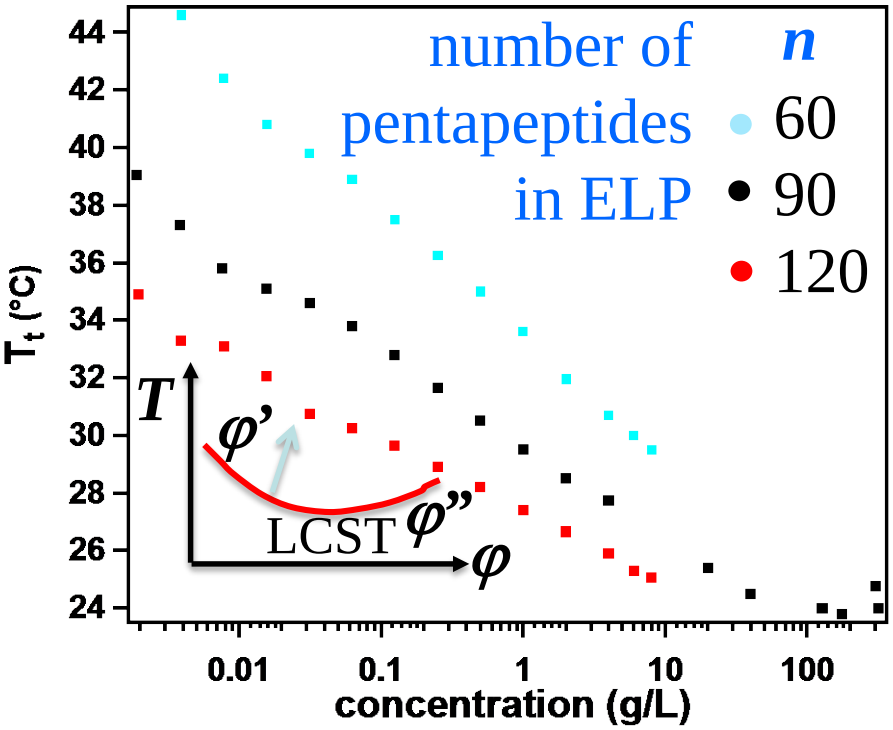
$$\ln(\phi''/\phi')/N^{2/3} \approx \gamma/(kT\phi''^{2/3})$$

Laurez, Adam, Carton, Raspaud 1997

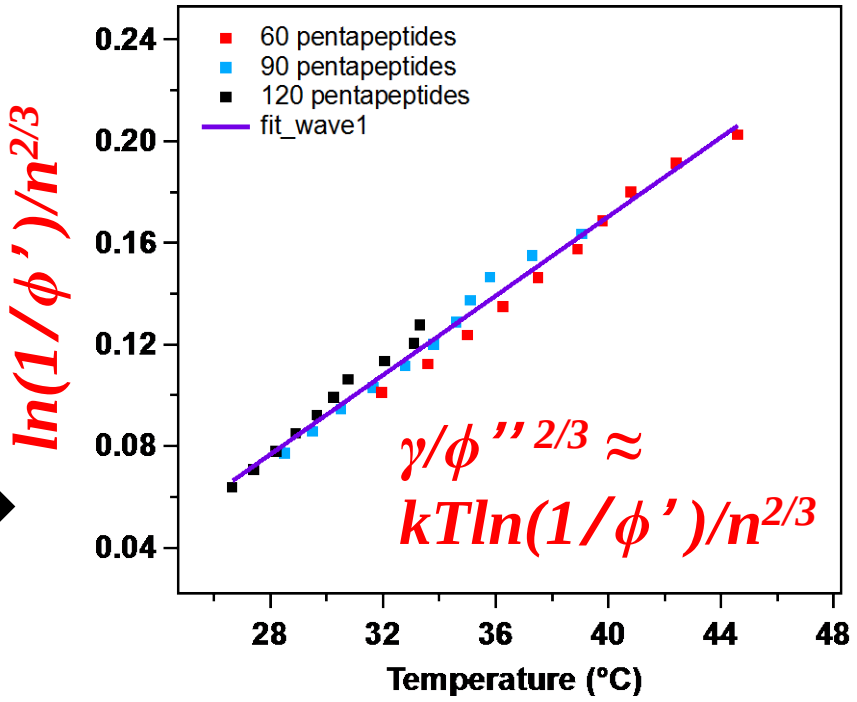
At higher T solubility of PS in heptane is higher and PS surface tension γ is lower.

T-Dependence of Surface Tension γ of Hydrophobic Block

φ' - branch of phase boundary $T(\varphi)$



Surface tension γ of ELP



$$\frac{\gamma}{\phi''^{\frac{2}{3}}} = \frac{kT}{nm^2}\left(\frac{0.00733}{K}\times T - 2.13\right)$$

Surface tension γ is ***n*-independent** and **very low** for a hydrophobic polymer with a dense sediment, which is possibly due to surfactant-like nature of pentapeptide repeat unit.

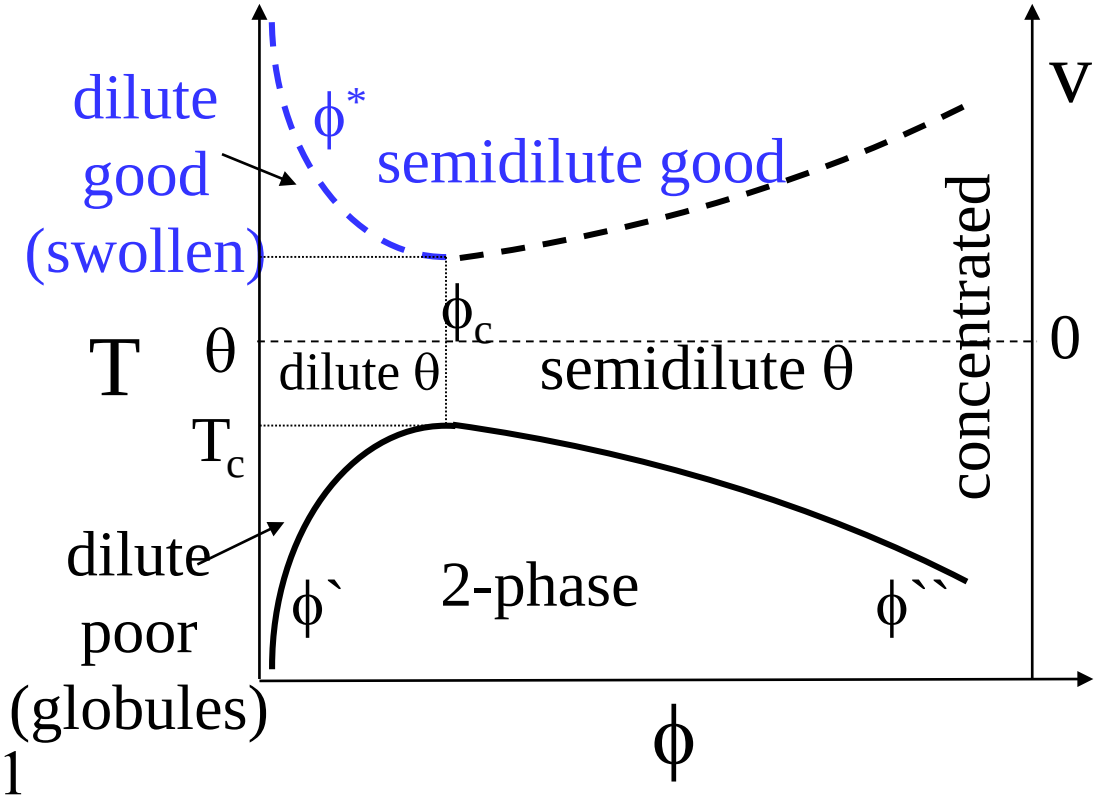
Good Solvent

Swollen chain size in dilute solutions

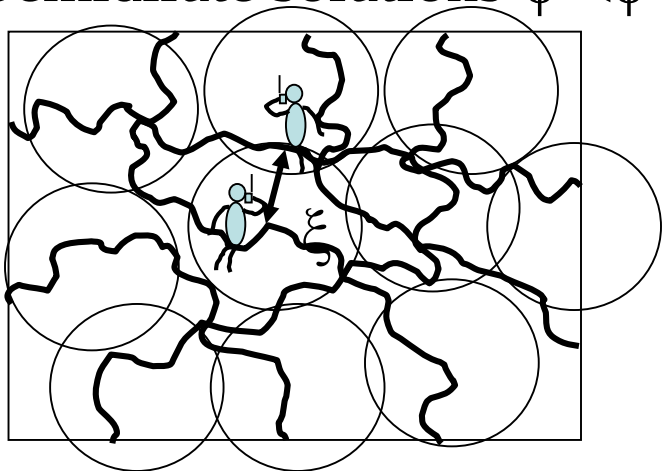
$$R \approx b\left(\frac{\mathrm{v}}{b^3}\right)^{1/5} N^{3/5}$$

Overlap concentration

$$\phi^* \approx \frac{Nb^3}{R^3} \approx \left(\frac{b^3}{\mathrm{v}}\right)^{3/5} N^{-4/5}$$



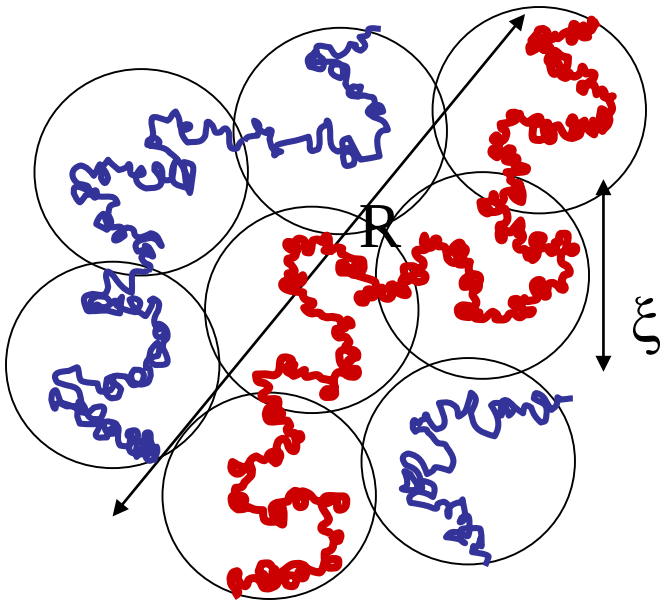
Semidilute solutions $\phi^* < \phi << 1$



Correlation length ξ

Distance from a monomer to nearest monomers on neighboring chains.

Correlation Length



For $r < \xi$ monomers are surrounded by solvent and monomers from the same chain.

The properties of this section of the chain of size ξ are the same as in dilute solutions.

$$\xi \approx b\left(\frac{\mathrm{v}}{b^3}\right)^{1/5} g^{3/5}$$

g – number of monomers inside a correlation volume, called correlation blob.

Correlation blobs are at overlap $\phi \approx \dfrac{gb^3}{\xi^3}$

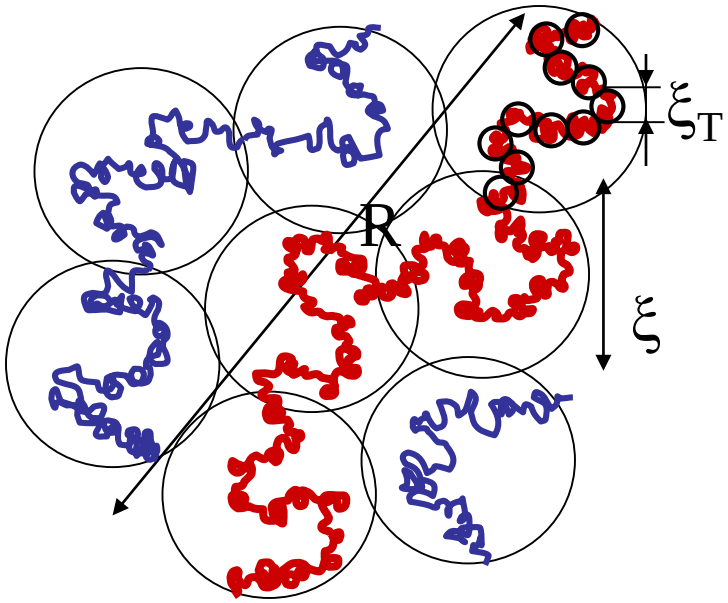
$$\xi \approx b\left(\frac{b^3}{\mathrm{v}}\right)^{1/4} \phi^{-3/4}$$

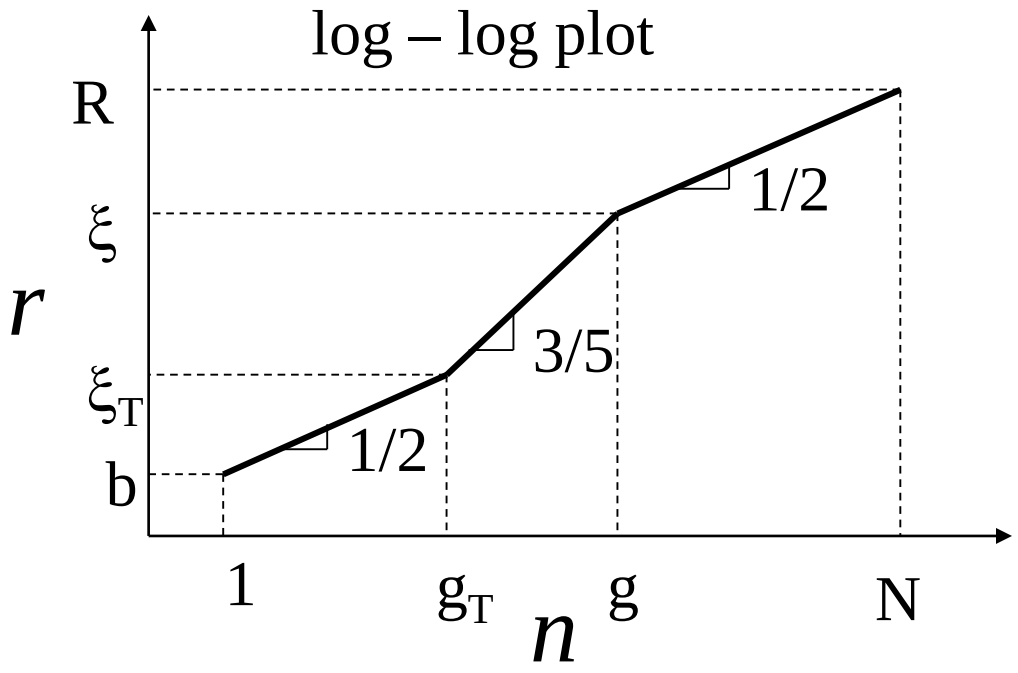
For $r > \xi$ sections of neighboring chains overlap and screen each other.

On length scales $r > \xi$ polymers are almost ideal chains - melt with N/g effective segments of size ξ.

$$R \approx \xi\left(\frac{N}{g}\right)^{1/2} \approx b\left(\frac{\mathrm{v}}{b^3\phi}\right)^{1/8} N^{1/2}$$

Semidilute Good Solvent





On length scales less than thermal blob ξ_T chain is ideal because excluded volume interactions are weaker than kT. $r \sim n^{1/2}$

On length scales larger than ξ_T but smaller than correlation length ξ excluded volume interactions are strong enough to swell the chain. $r \sim n^{3/5}$

On length scales larger than correlation length ξ excluded volume interactions are screened by surrounding chains. $r \sim n^{1/2}$

Concentrated Solutions

Correlation length ξ decreases with concentration, while thermal blob size ξ_T is independent of concentration.

At concentration ϕ^{**} the two lengths are equal $\xi \approx \xi_T$ and intermediate swollen regime disappears.

$$\phi^{**} \approx \frac{v}{b^3} \qquad \xi \approx b\left(\frac{b^3}{v}\right)^{1/4} \phi^{-3/4} \approx \frac{b^4}{v} \approx \xi_T$$

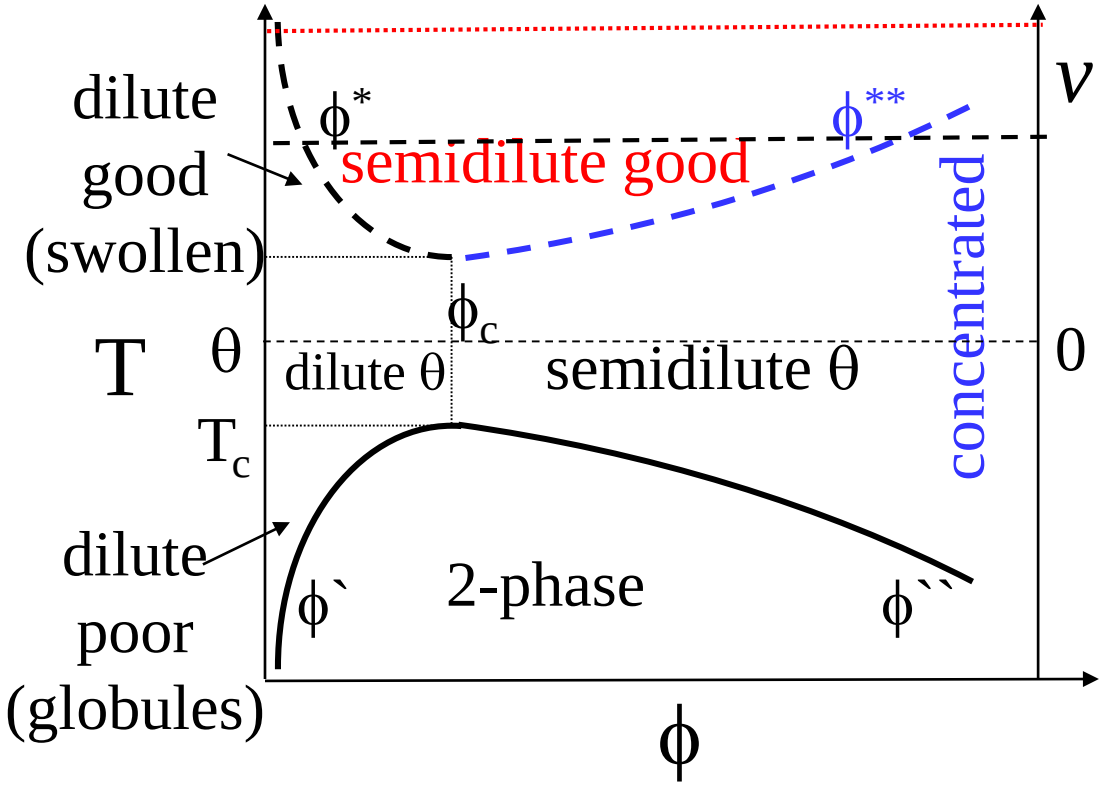
This concentration is analogous to $\phi^{"}$ in poor solvent at which two- and three-body interactions are balanced.

In concentrated solutions chains are ideal at all length scales.

On length scales less than correlation length ξ chains are ideal because excluded volume interactions are weaker than kT.

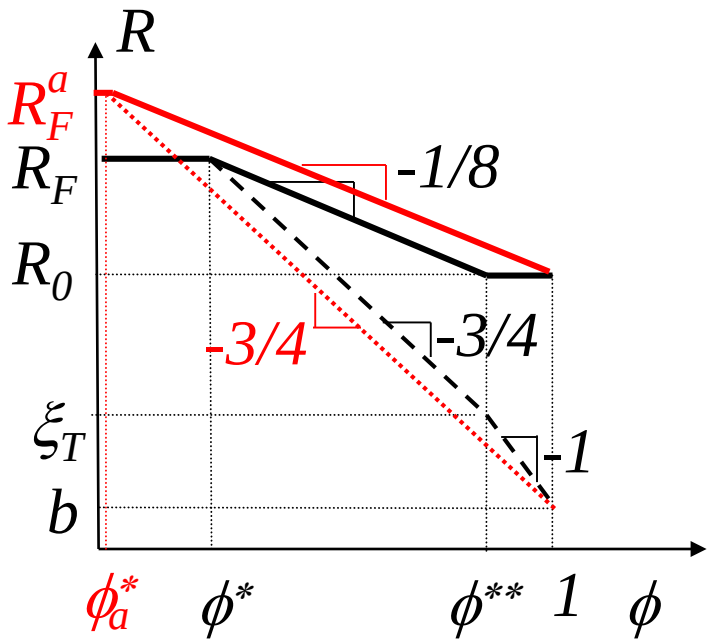
On length scales larger than ξ chains are ideal because excluded volume interactions are screened by surrounding chains.

Semidilute Good Solvent Solutions



$$R \approx R_0 \left(\frac{\phi}{\phi^{**}} \right)^{-1/8}$$

for $\phi^* < \phi < \phi^{**}$



In athermal solvent $\nu \approx b^3$ $\xi_T \approx b$

$$\xi \approx \frac{b}{\phi^{3/4}}$$

$$R \approx \frac{bN^{1/2}}{\phi^{1/8}}$$

$\phi_a^* \approx N^{-4/5}$

$\phi^{**} \approx 1$

Osmotic Pressure

In dilute solutions $\phi < \phi^*$ - van't Hoff Law $\Pi \approx \frac{kT}{b^3}\frac{\phi}{N}$

Osmotic pressure Π in semidilute solutions $\phi > \phi^*$ is a stronger function of concentration

$$\Pi \approx \frac{kT}{b^3}\frac{\phi}{N} f\left(\frac{\phi}{\phi^*}\right) \qquad f\left(\frac{\phi}{\phi^*}\right) \approx \begin{cases} 1 \text{ for } \phi < \phi^* \\ (\phi/\phi^*)^y \text{ for } \phi > \phi^* \end{cases}$$

Osmotic pressure in semidilute solutions

$$\Pi \approx \frac{kT}{b^3}\frac{\phi}{N}\left(\frac{\phi}{\phi^*}\right)^y \approx \frac{kT}{b^3}\phi^{1+y}\left(\frac{\mathrm{v}}{b^3}\right)^{3y/5} N^{4y/5-1}$$

$$\phi^* \approx \frac{Nb^3}{R^3} \approx \left(\frac{b^3}{\mathrm{v}}\right)^{3/5} N^{-4/5}$$

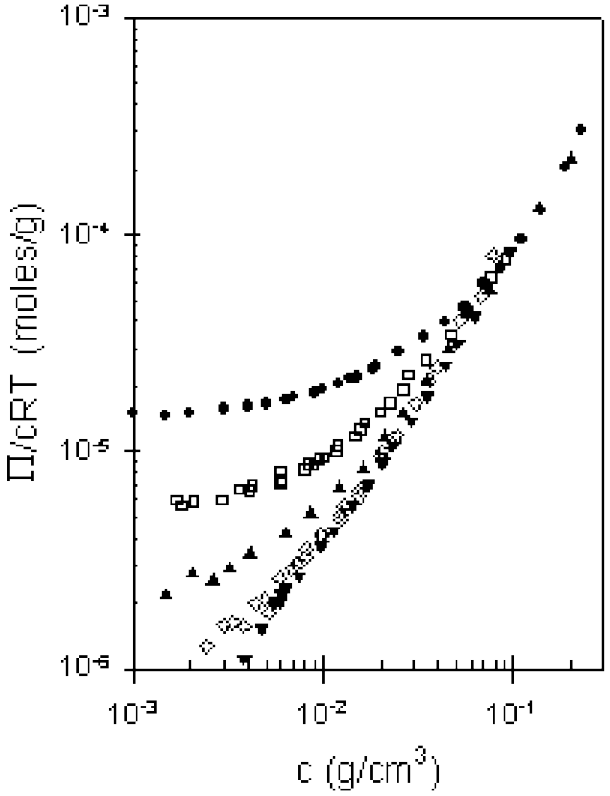
is independent of chain length ($4y/5-1=0$). $y=5/4$

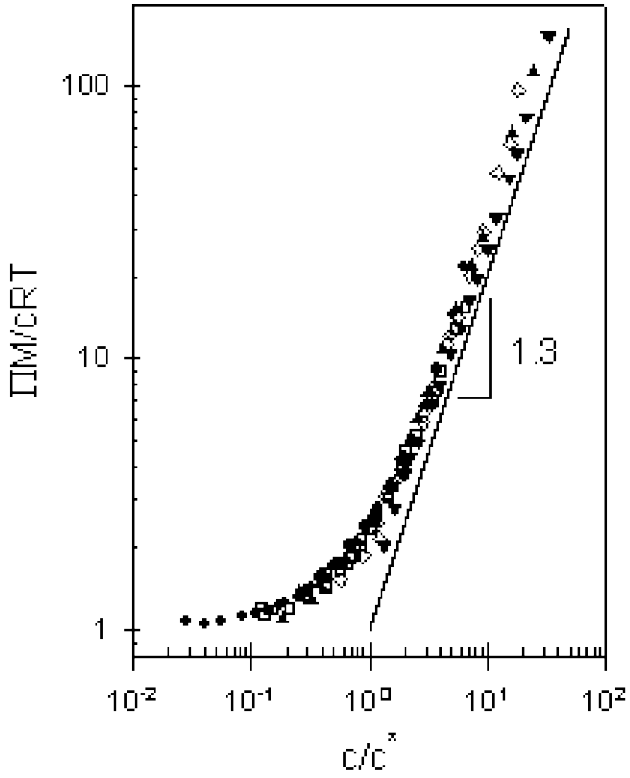
$$\Pi \approx \frac{kT}{b^3}\left(\frac{\mathrm{v}}{b^3}\right)^{3/4} \phi^{9/4} \approx \frac{kT}{\xi^3}$$

Neighboring blobs repel each other with energy of order kT.

Concentration Dependence of Osmotic Pressure

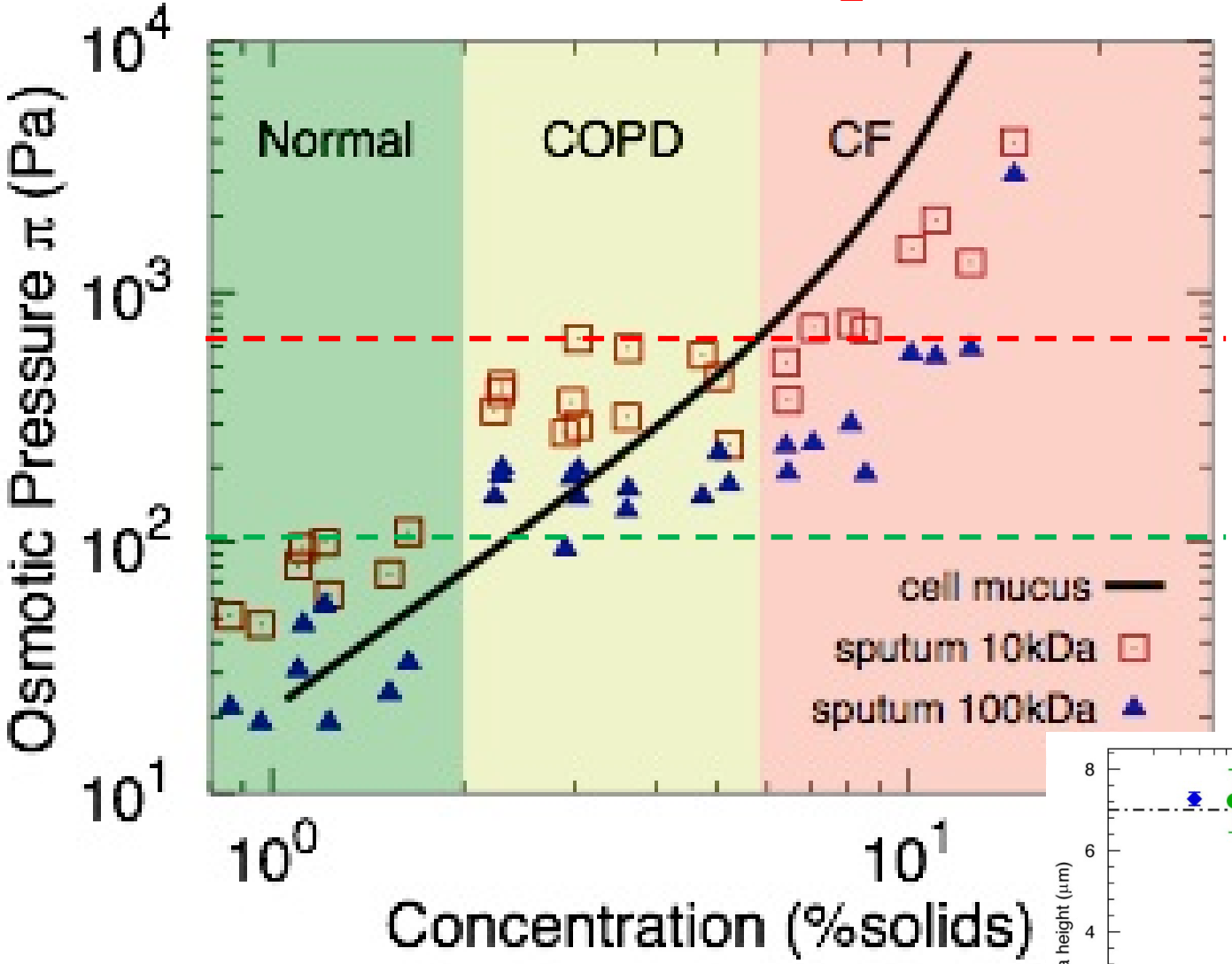
$$\frac{\Pi b^3 N}{kT\phi} \approx f\left(\frac{\phi}{\phi^*}\right) \approx 1 + \left(\frac{\phi}{\phi^*}\right)^{1.3}$$

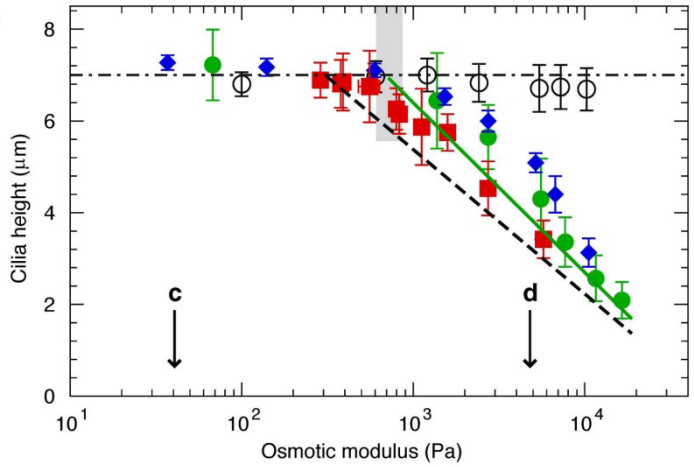




Poly(α-methylstyrene) in toluene at 25 °C
Noda et al, Macromol. **16**, 668, 1981

Osmotic Pressure of Sputum From Patients

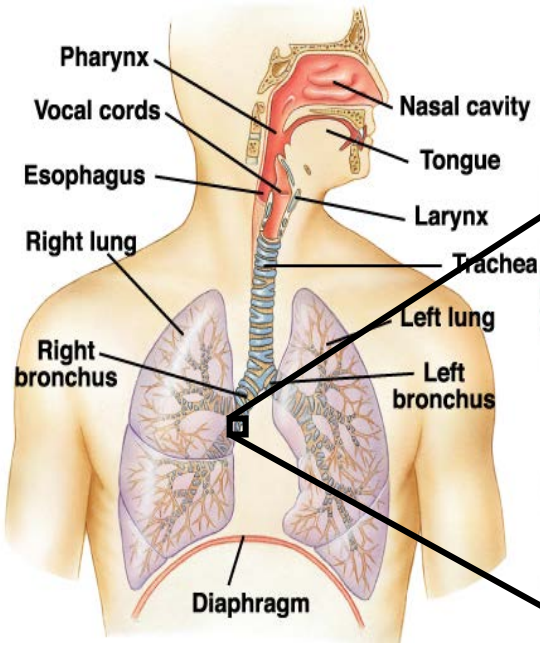


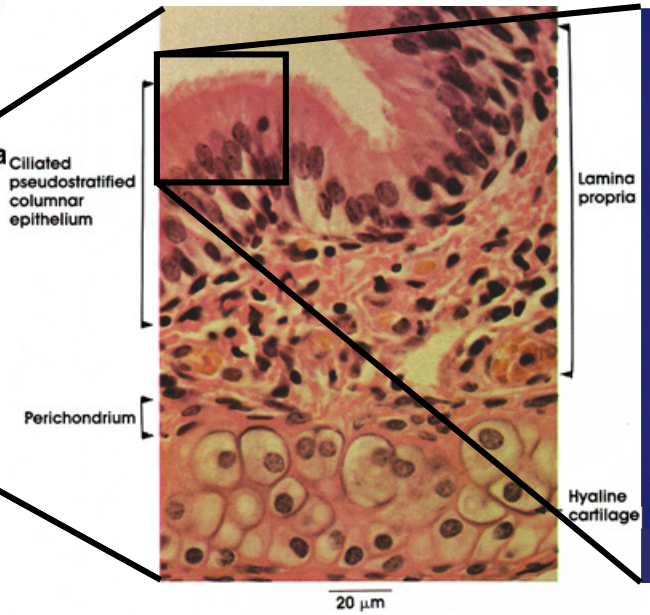


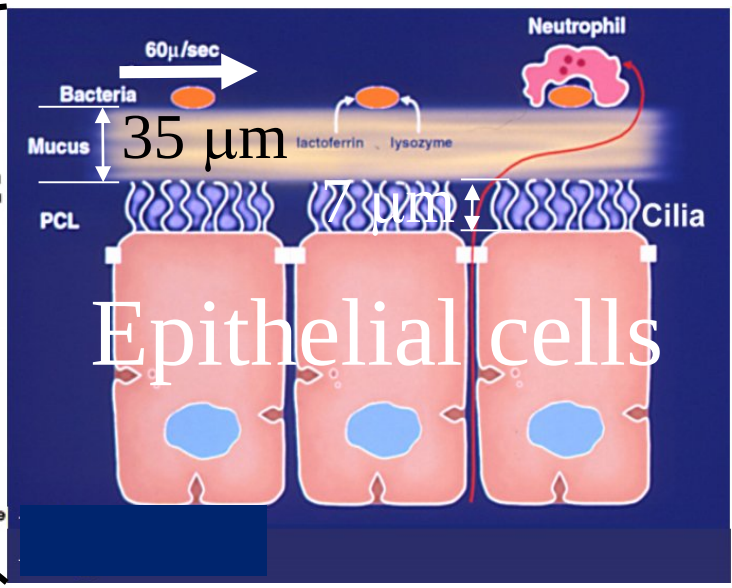
Science 337, 937-941 (2012)

Airway Surface Layer (ASL)

Airway surface layer consists of two sublayers – mucus and periciliary layer (PCL).



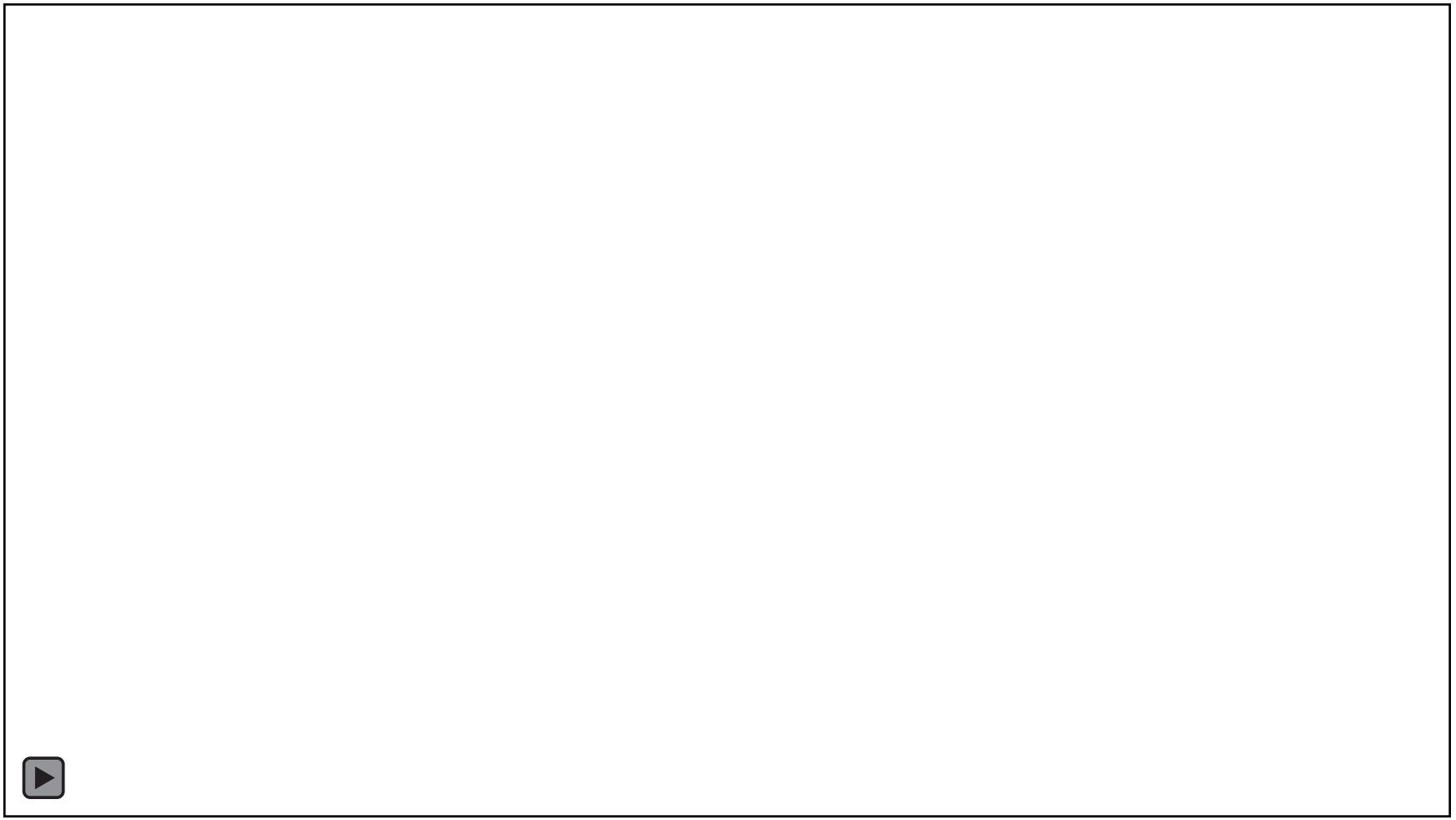




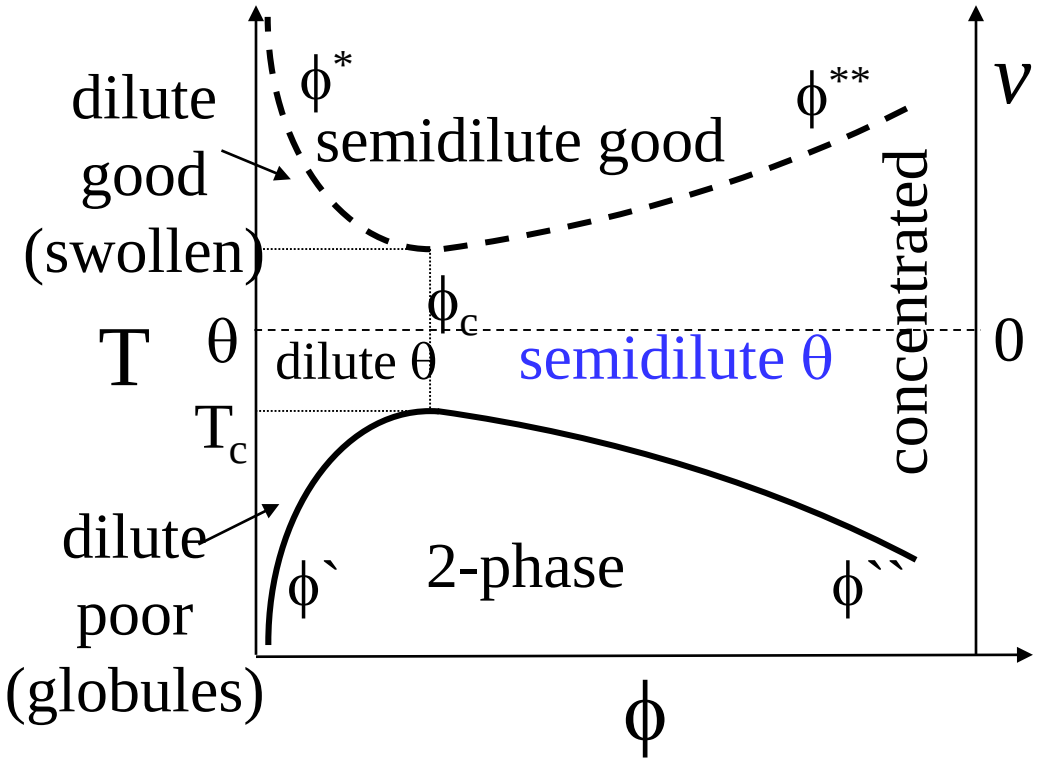
Muco-Ciliary Escalator

The mucus bathes the surface of PCL containing cilia which beat regularly and move the mucus to the throat. Any particles that have got through the upper defenses are trapped in this mucus, moved upwards and expelled by coughing or swallowing.

Osmotically-Driven Hydration & Dehydration of ASL

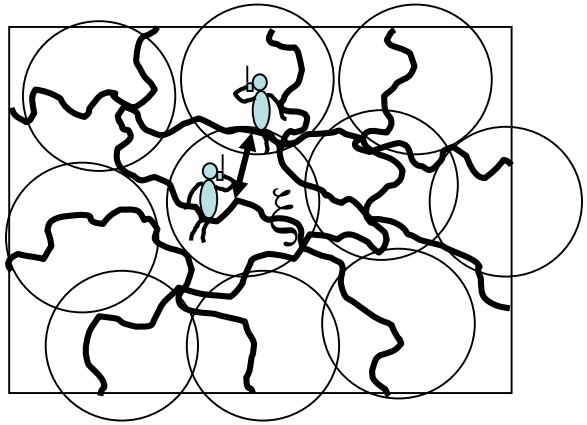


Semidilute Theta Solutions



Chains are almost ideal

$$R \approx bN^{1/2}$$



$$g \approx \left(\frac{\xi}{b}\right)^2$$

Correlation blobs are space-filling

$$\phi \approx \frac{b^3 g}{\xi^3} \approx \frac{b^3 (\xi/b)^2}{\xi^3} \approx \frac{b}{\xi}$$

$$\xi \approx \frac{b}{\phi}$$

Osmotic Pressure in Semidilute Theta Solutions

Mean-field prediction $\Pi = \frac{kT}{b^3}\left(\frac{\phi}{N} + \frac{w}{b^6}\phi^3 + \ldots\right)$

First term (van't Hoff law) is important in dilute solutions

Three-body term is larger than linear in semidilute solutions $\phi > \phi^* \approx 1/N^{1/2}$ $\quad \Pi = \frac{kT}{b^3}\phi^3$

Scaling Theory

$$\Pi \approx \frac{kT}{b^3}\frac{\phi}{N}h\left(\frac{\phi}{\phi^*}\right) \qquad h\left(\frac{\phi}{\phi^*}\right) \approx \begin{cases} 1 \text{ for } \phi < \phi^* \\ (\phi/\phi^*)^y \text{ for } \phi > \phi^* \end{cases}$$

Osmotic pressure in semidilute θ–solutions

$$\Pi \approx \frac{kT}{b^3}\frac{\phi}{N}\left(\frac{\phi}{\phi^*}\right)^y \approx \frac{kT}{b^3}\phi^{1+y}N^{y/2-1}$$

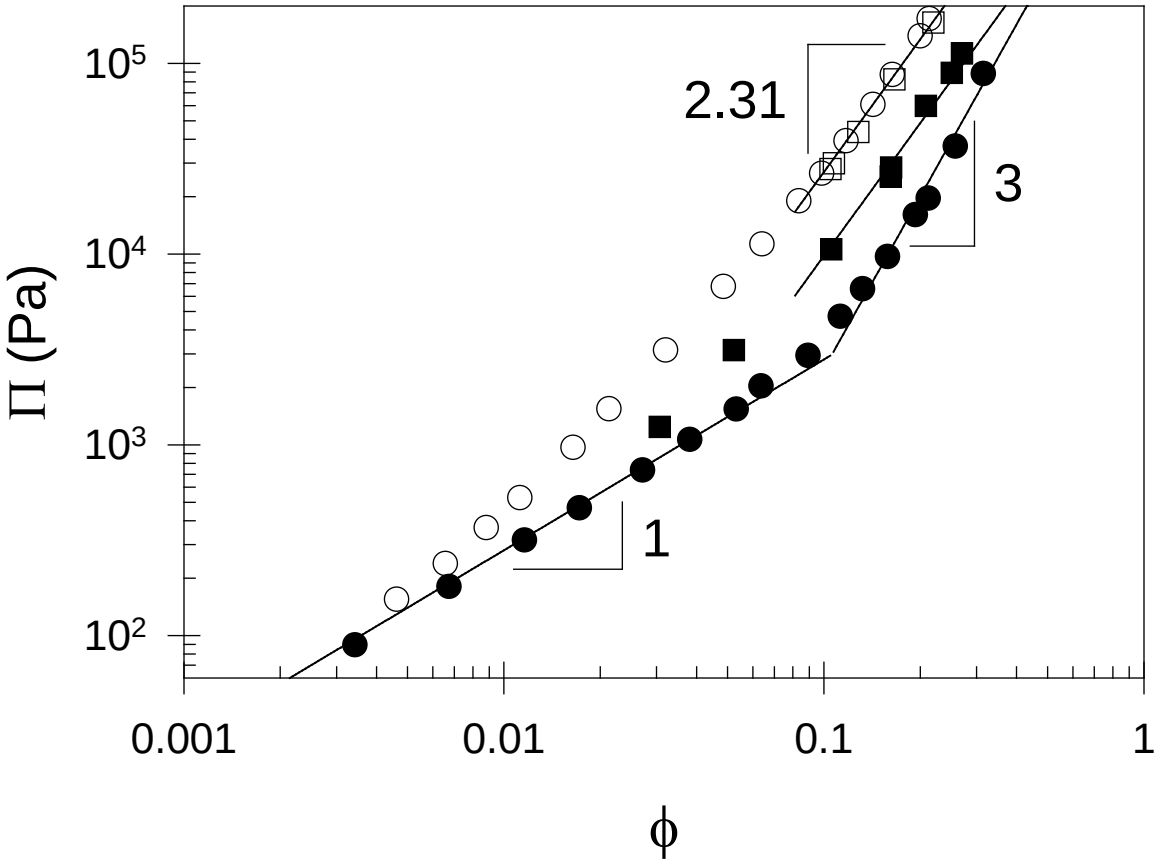
is independent of chain length ($y/2\text{-}1=0$). $y=2$ $\quad \Pi \approx \frac{kT}{b^3}\phi^3 \approx \frac{kT}{\xi^3}$ $\quad \xi \approx \frac{b}{\phi}$

Overlap concentration

$$\phi_\theta^* \approx \frac{Nb^3}{R^3} = \frac{1}{\sqrt{N}}$$

kT per correlation blob ξ^3 – same as mean field

Osmotic Pressure



Polyisobutylene in benzene at θ=24.5 °C (filled circles), in benzene at 50 °C (filled squares), in cyclohexane at 30 °C (open circles) and at 8 °C (open squares)
Flory and Daoust J. Polym. Sci. **25**, 429, 1957

$$\xi \approx \frac{b}{\phi}$$

$$\Pi \approx \frac{kT}{\xi^3} \approx \frac{kT}{b^3}\phi^3$$

Correlation length in semidilute θ-solvents is of the order of the distance between 3-body contacts.

Number density of n-body contacts ~ ϕ^n/b^3

Distance between n-body contacts in 3-dimensional space

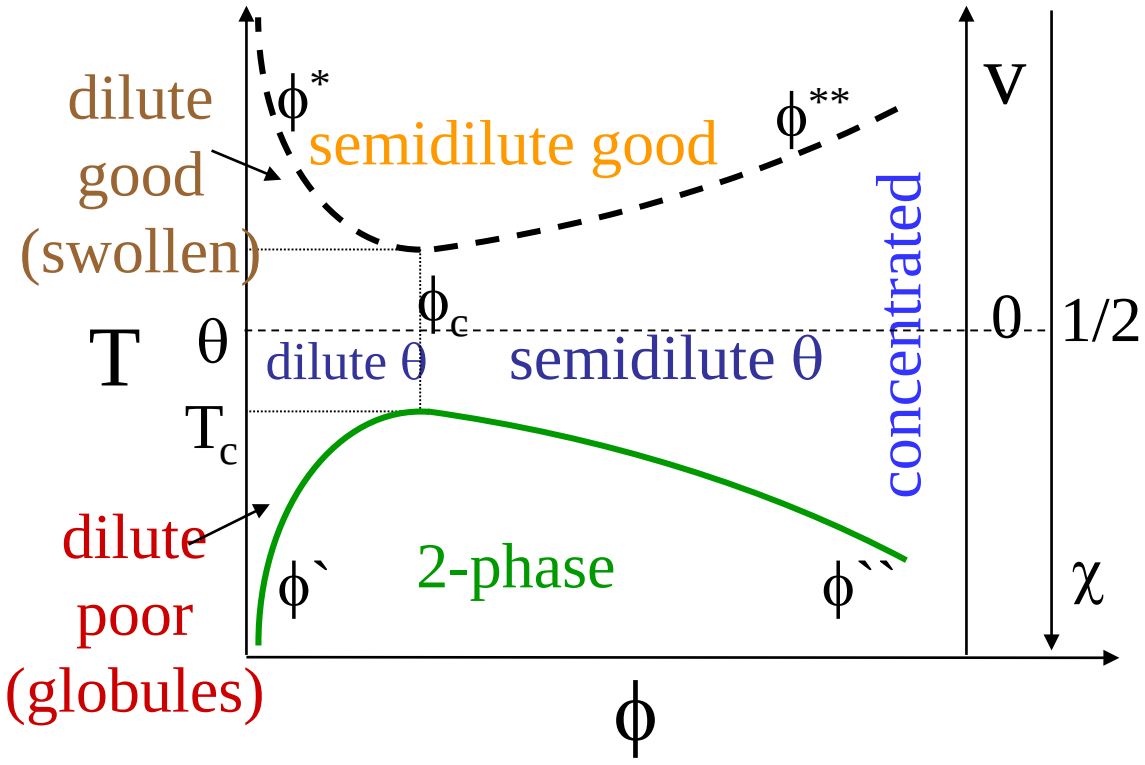
$$r_n \approx b\phi^{-n/3}$$

Quiz # 6

What is the meaning of correlation length in semidilute theta solutions?

How different are semidilute theta solutions from ideal solutions of ideal chains?

Summary of Polymer Solutions



In poor solvent part of the diagram binodal separates 2-phase from 2 single phase regions:

Dilute globules at low concentrations $\phi < \phi'$

Concentrated solutions with overlapping almost ideal chains at $\phi > \phi''$

Near θ–temperature there are dilute and semidilute θ-regimes with almost ideal chains.

Dilute good solvent regime with swollen chains at $\phi < \phi^*$ and $v > 0$.

Semidilute good solvent regime at $\phi^* < \phi < \phi^{**}$ with chains swollen at intermediate length scales shorter than correlation length ξ.

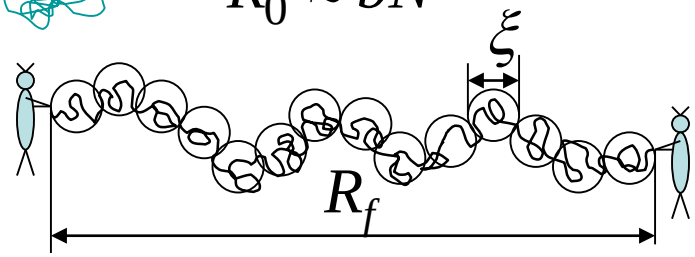
Osmotic pressure in semidilute solutions is kT per correlation volume ξ^3.

Polymers Under Tension

Ideal chain

$$R_0 \approx bN^{1/2}$$

Unperturbed size



Tension blobs (Pincus blobs) of size ξ contain g monomers

On length scales up to ξ chains are almost unperturbed

$$\xi \approx bg^{1/2}$$

On larger length scales they are stretched into arrays of Pincus blobs

$$R_f \approx \xi N/g \approx Nb^2/\xi \approx R_0^2/\xi$$

Size of Pincus blobs

$$\xi \approx R_0^2/R_f$$

Tension force is on the order of kT divided by the blob size ξ

$$f \approx kT/\xi \approx \left(kT/R_0^2\right)R_f$$

Real chain

$$R_F \approx bN^{3/5}$$

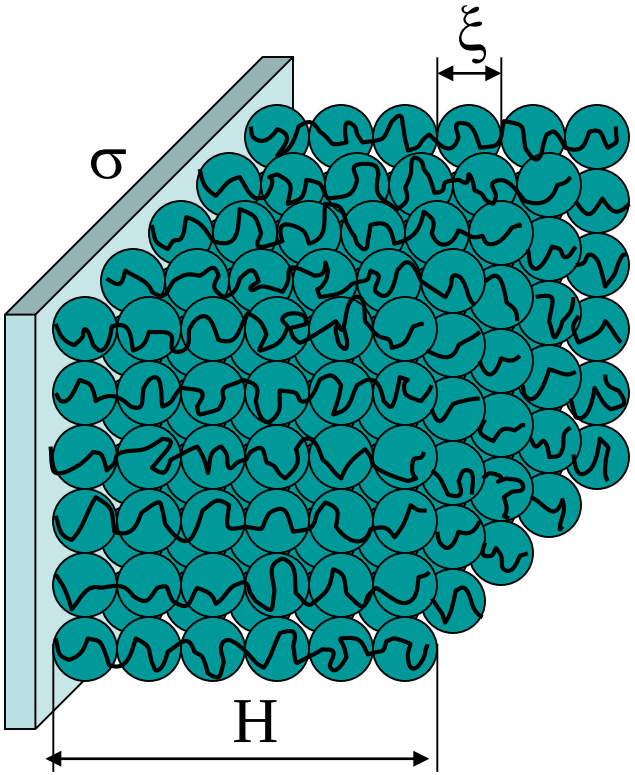
$$\xi \approx bg^{3/5}$$

$$R_f \approx \xi N/g \approx Nb^{5/3}/\xi^{2/3} \approx R_F^{5/3}/\xi^{2/3}$$

$$\xi \approx R_F^{5/2}/R_f^{3/2}$$

$$f \approx kT/\xi \approx \left(kT/R_F^{5/2}\right)R_f^{3/2}$$

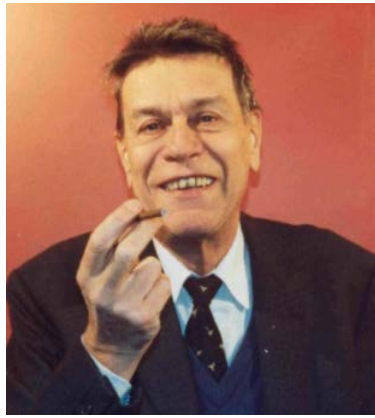
Alexander – de Gennes Brush



Grafting density σ –number of chains per unit area.

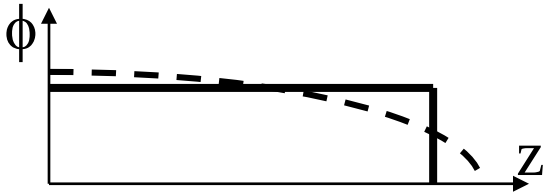
Distance between sections of chains

$$\xi = \sigma^{-1/2}$$



Number of monomers per blob

$$g \sim \xi^{1/\nu} \sim \sigma^{-1/(2\nu)}$$



Thickness of the brush $H \sim \xi N/g \sim N\sigma^{(1-\nu)/(2\nu)}$

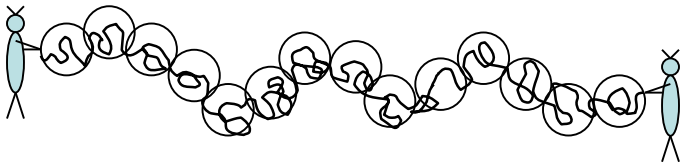
In θ-solvent $H \sim N\sigma^{1/2}$ In good solvent $H \sim N\sigma^{1/3}$

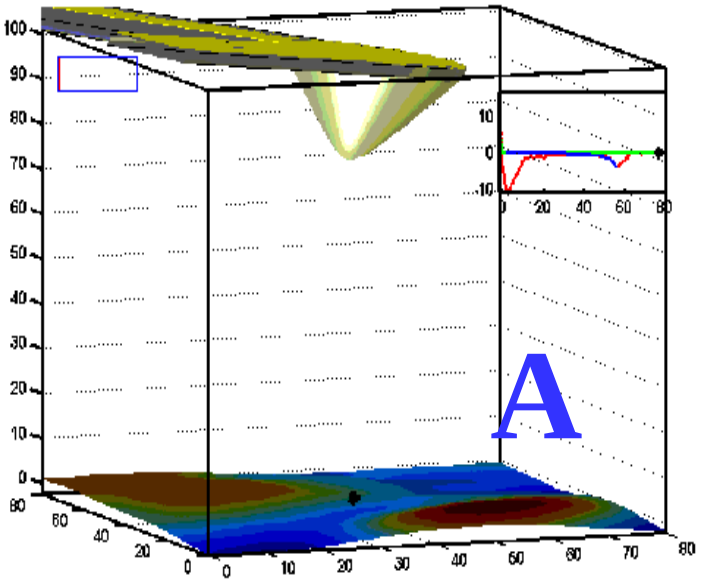
Energy per chain $E_{chain} \sim kT\, N/g \sim kTN\sigma^{1/(2\nu)}$

Energy per unit volume $\dfrac{E_{chain}}{V} \approx E_{chain}\dfrac{\sigma}{H} \approx kT\dfrac{N}{g}\dfrac{\sigma}{H} \approx kT\dfrac{\sigma}{\xi} \approx \dfrac{kT}{\xi^3} \approx \Pi$

Quiz #7

Compare and contrast the average bond length in a polymer chain **A** under tension



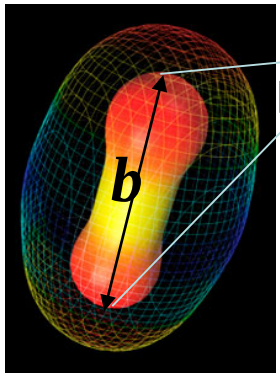


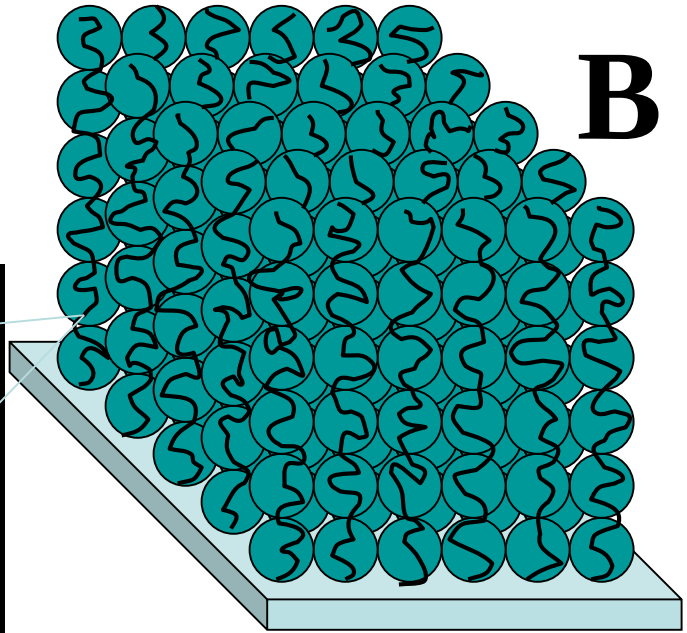
with the average bond length in an extended polymer chain **B** – same polymer under the same extension – but due to lateral compression in a polymer brush.

Bonds in chain **A** are elongated.

What about bonds in chain **B**?

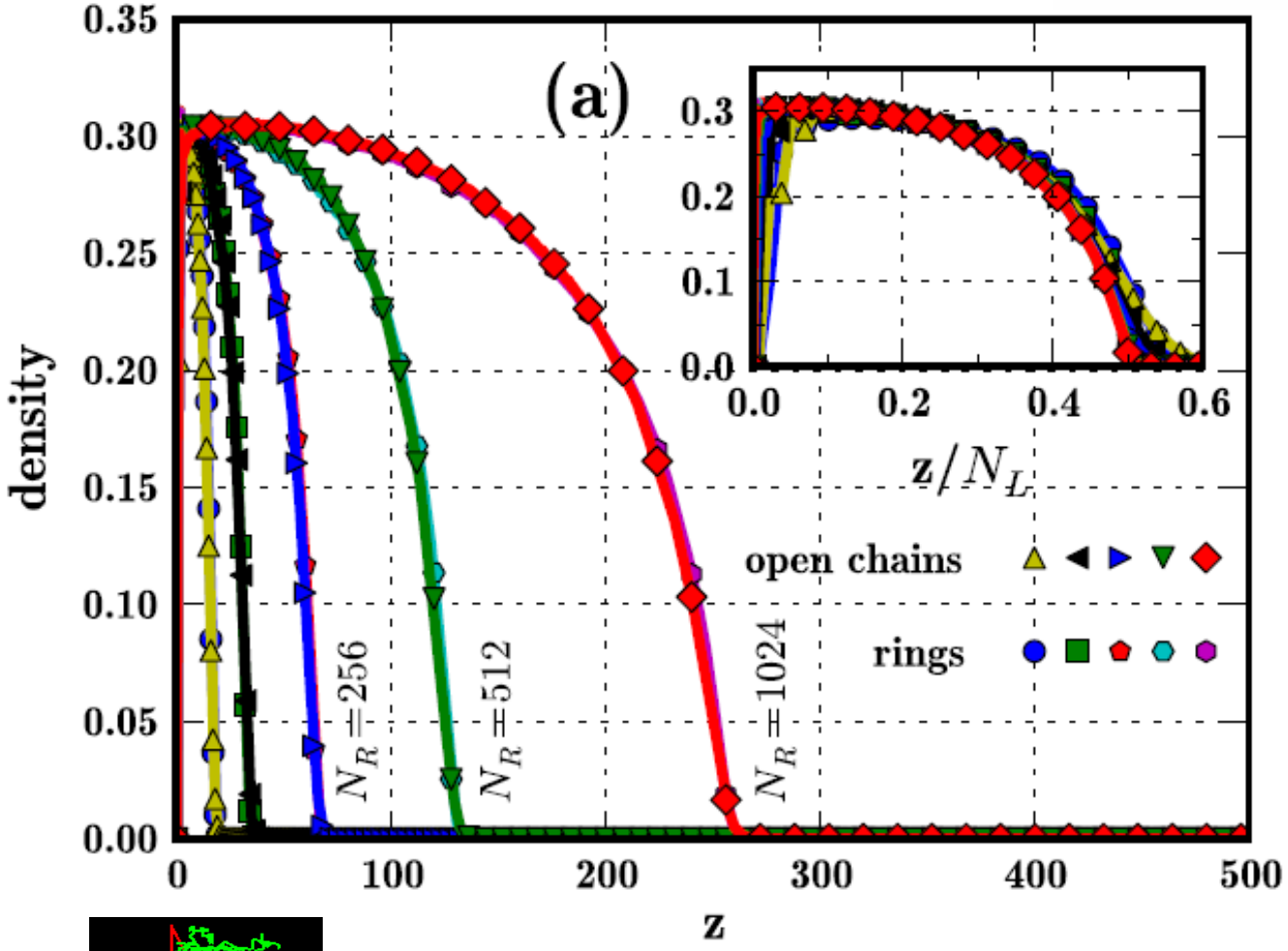
Is bond length b of chain B larger or smaller than b_0 of a free chain?

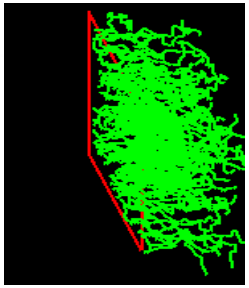




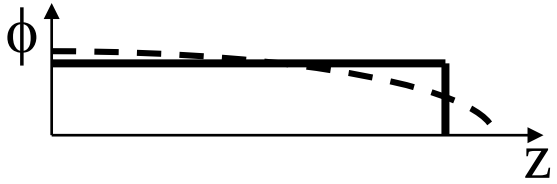
Monomer Density Profile

EPL, **95** (2011) 28003





Chain ends are distributed throughout the brush

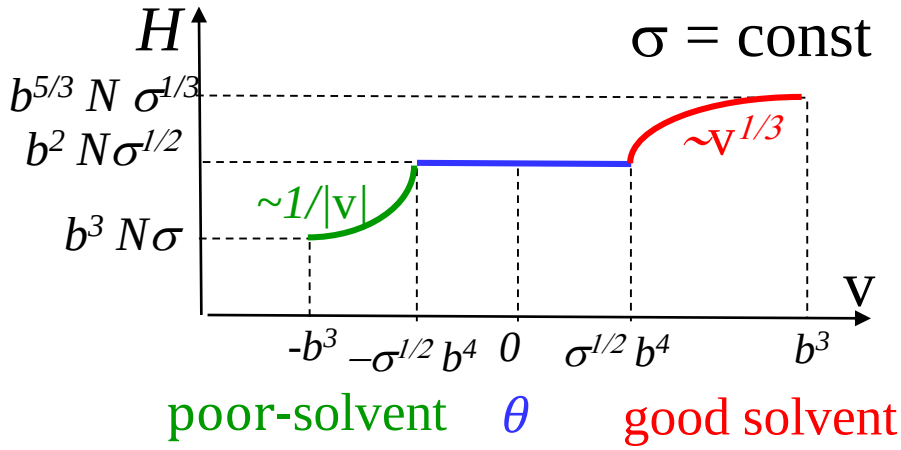


Parabolic density profile

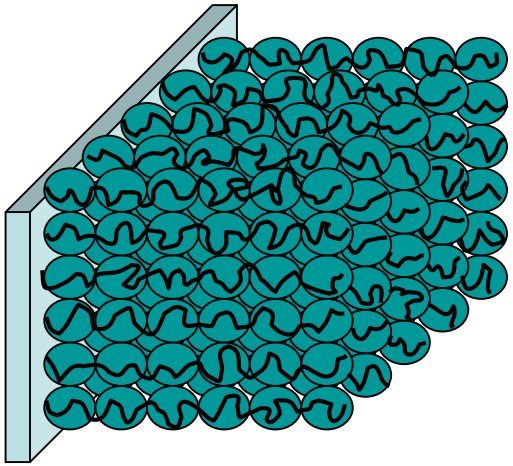
Semenov 1985

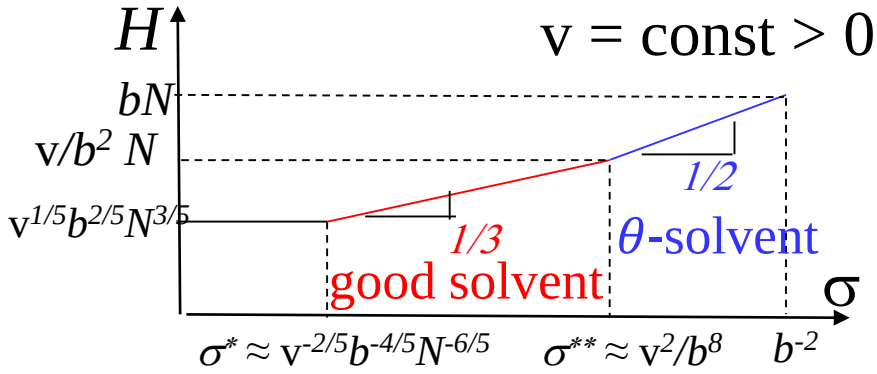
Homework Assignment # 1

Verify the solvent quality dependence of brush thickness

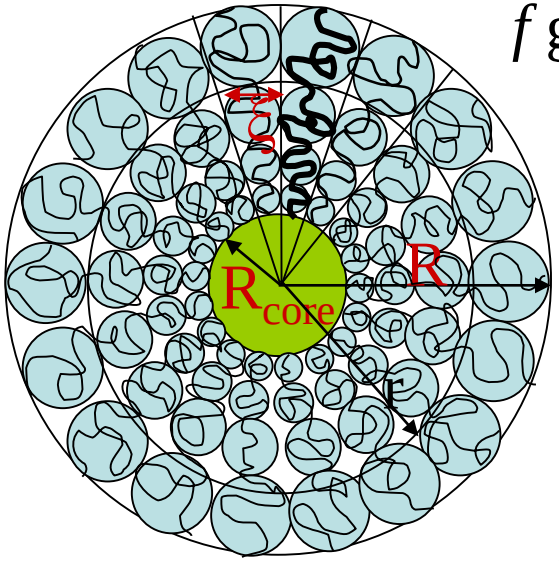


and grafting density dependence of brush thickness





Spherical Brush in a Good Solvent



f grafted polymers $4\pi r^2/f$ – area per polymer at r

Correlation length increases linearly with r

$$\xi \sim r/f^{1/2}$$

Volume fraction $\phi \sim \xi^{-4/3} \sim (f^{1/2}/r)^{4/3}$

Number of monomers in the brush

$$fN = \int_{R_{core}}^{R} 4\pi r^2 \phi(r) dr \approx f^{2/3} R^{5/3}$$

Flory Theory

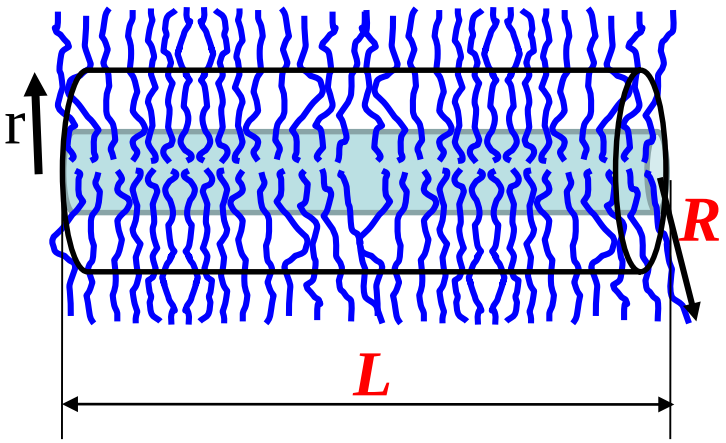
Brush size $R \sim f^{1/5} N^{3/5}$

$$F \approx kT\left(f\frac{R^2}{Nb^2} + b^3\frac{(fN)^2}{R^3}\right)$$

Free energy per chain

$$\frac{F}{f} \approx kT\int_{R_{core}}^{R}\frac{dr}{\xi} \approx kT\int_{R_{core}}^{R} f^{1/2}\frac{dr}{r} \approx kTf^{1/2}ln\left(\frac{R}{R_{core}}\right)$$

Cylindrical Brush in a Good Solvent



σ grafted polymers per unit length

$2\pi r$ – area at distance r per unit length

$2\pi r/\sigma$ – area per polymer at distance r

Correlation length $\xi \sim (r/\sigma)^{1/2}$

Volume fraction $\phi \sim \xi^{-4/3} \sim (\sigma/r)^{2/3}$

Number of monomers in the brush per unit length

$$N\sigma = \int_{R_{core}}^{R} 2\pi r \phi(r) dr \approx \sigma^{2/3} R^{4/3}$$

Brush thickness $R \sim \sigma^{1/4} N^{3/4}$

Flory Theory $F \approx kT\left(L\sigma\frac{R^2}{Nb^2} + b^3\frac{(L\sigma N)^2}{LR^2}\right)$

Free energy per chain

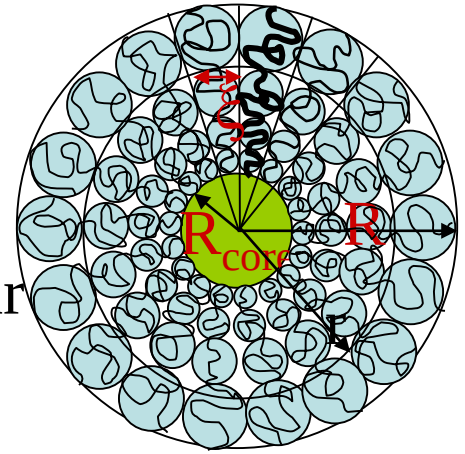
$$\frac{F}{kTL\sigma} \approx \int_{R_{core}}^{R} \frac{dr}{\xi} \approx \int_{R_{core}}^{R} \sigma^{1/2}\frac{dr}{r^{1/2}} \approx \sigma^{1/2}R^{1/2} \approx \sigma^{5/8}N^{3/8}$$

Homework Assignment # 2

Repeat the calculations for spherical and cylindrical brushes in θ-solvent

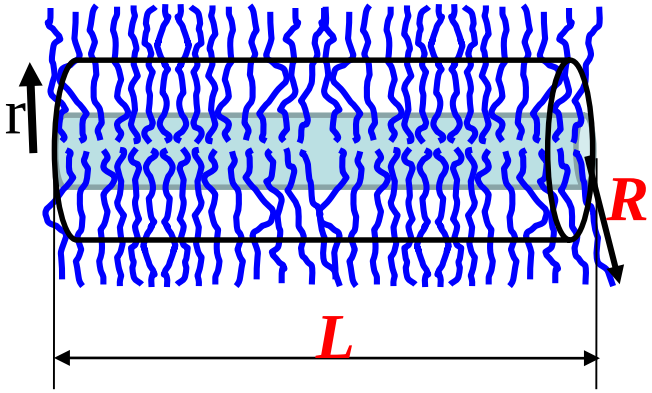
Using both scaling and Flory theory show that the size of the spherical brush in θ-solvent is

$$R \sim f^{1/4} N^{1/2}$$



but the free energy per chain in θ-solvent is similar to free energy of a spherical brush in good solvent

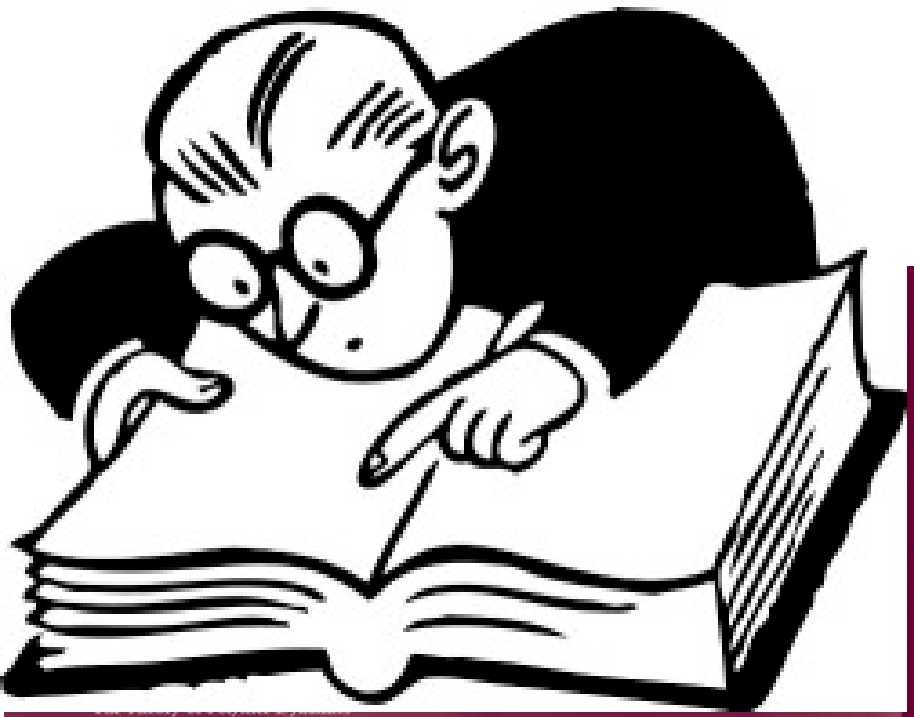
$$F/f \approx kT f^{1/2} ln(R/R_{core})$$



Using both scaling and Flory theory show that the size of the cylindrical brush in θ-solvent is

$$R \sim \sigma^{1/3} N^{2/3}$$

and the free energy per chain is $\dfrac{F}{kTL\sigma} \approx \sigma^{2/3} N^{1/3}$



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